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Review of groundwater monitoring data (2004 – 2010) from the Waihora well field, Lake Taupo catchment

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Review of groundwater monitoring data (2004 – 2010) from the Waihora well field, Lake Taupo catchment

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EXECUTIVE SUMMARY

Lincoln Ventures was contracted by Waikato Regional Council to provide a comprehensive review of groundwater level and chemistry data collected at two water table well (WTW) transects in the Waihora well field for the period 2004 – 2010. Land use at the site was relatively low intensity sheep and beef grazing as found widespread in the Lake Taupo catchment. The WTWs comprised relatively long screen lengths that intersected the groundwater table, hence yielded composite samples of groundwater drawn from a water column of variable thickness. In contrast, multilevel wells (MLWs) that were additionally installed in 2007 enabled sampling of discrete depth ranges of 50 cm thickness, which allowed for detection of vertical groundwater chemistry stratification. Data from these MLWs have been used to facilitate the interpretation of the WTW data. A discussion of the implications of the different well types on monitoring data has been included in this report.

Summary of WTW groundwater level data:

- The mean depth of the vadose zone ranged from 2.1 to 2.6 m at the Lower Transect and from 3.9 to > 8.3 m at the Upper Transect.
- The mean groundwater level at a particular well (relative to mean sea level) was largely determined by its distance from the wetland, which constitutes a local groundwater discharge area. However, some unexplained gradients were observed at both ends of the Upper Transect, where water level gradients inverse to the topographic gradient were identified.
- The extent of temporal water level variation was determined by the distance to the wetland and by the hydraulic properties of the lithological strata surrounding the well screen. Hence, water level amplitudes were smaller at the Lower Transect (1.5 – 1.8 m) than at the Upper Transect (2.2 – 4.9 m). The smaller amplitudes at the Upper Transect were observed where the well was entirely screened within the Taupo Ignimbrite stratum. The greatest amplitudes occurred where the well penetrated into the underlying Palaeosol and Oruanui Ignimbrite strata, reflecting the lower effective storage characteristics of these materials.

Summary of WTW groundwater chemistry data:

- Overall, only moderate variability in groundwater chemistry was exhibited, with exception of groundwater at the peripheral wells of the Upper Transect (WR3, WR6, WR10) where some large temporal variations have been recorded. Only groundwater pH appears to have exhibited an obvious long-term trend over the monitoring period.
- The overall mean nitrate nitrogen concentration of all 682 groundwater samples analysed in near-monthly intervals between 2004 and 2010 was 2.07 mg/L; the median was lower at 1.53 mg/L. Nitrate nitrogen concentrations were on average higher and more variable at the Upper Transect (2.38 ± 2.90 mg/L) than at the Lower Transect (1.79 ± 1.17 mg/L).
- Assuming the overall mean nitrate nitrogen concentration of 2.07 mg/L best describes the concentration of recharging groundwater and using the mean annual recharge volume estimate of 697 mm, mean annual nitrate nitrogen input from the vadose zone can be estimated as 14 kg/ha. As circumstantial evidence suggests that the mean nitrate concentration of the data set has already been reduced by groundwater denitrification, it would appear that the actual leaching losses from the root zone may have been markedly higher than the 9 kg/ha estimated using the OVERSEER nutrient balancing model.

- With a mean of 0.10 mg/L, ammonia nitrogen concentrations equated to only 5% of the mean nitrate nitrogen concentration. The median was even smaller (0.03 mg/L), underlining the insignificance of ammonia from a nitrogen mass loss as well as an eco-toxicity point of view.
- pH levels varied between 4.8 and 6.6; with an overall mean of 5.8. The mean pH was tentatively lower at the Upper Transect (pH 5.8) than at the Lower Transect (pH 5.9). On average, pH increased over the monitoring period by 0.7 pH units; most of this increase occurred during 2006/07.
- Electrical conductivity showed less spatial and temporal variation than most other parameters. The overall mean was 97 µS/cm. The higher mean of the Upper Transect (105 µS /cm) compared to the Lower Transect (89 µS /cm) was largely due to the consistently higher values observed at one well (WR3 mean = 184 µS /cm).
- The overall mean concentration of dissolved inorganic carbon (DIC) was 5.0 mg/L. The mean DIC concentration at the Upper Transect (6.9 mg/L) was approx. 60% higher than at the Lower Transect (4.4 mg/L).
- DOC concentrations were substantially lower than DIC concentrations. The overall mean DOC concentration was 3.3 mg/L, with a standard deviation of 5.6 mg/L. This high variation is also reflected in the overall median of only 2.0 mg/L. The mean DOC concentration of the Upper Transect samples was nearly three times as high (5.0 mg/L) than the mean DOC concentration of the Lower Transect samples (1.8 mg/L).

<u>Summary of supplementary MLW data:</u>

- By analysing a suite of redox sensitive parameters it was established that strong redox-gradients can exist in shallow groundwater within the depth range of the WTWs. While groundwater at the top of the saturated zone was predominantly oxidised, reduced groundwater, depleted in dissolved oxygen and nitrate nitrogen, occurred at several MLW locations at somewhat greater depth.
- Reduced groundwater occurred consistently at the base of the Taupo Ignimbrite stratum at those locations where woody debris from the most recent Taupo eruption (1.8 ka BP) was present. This finding indicated that this debris is still a carbon source available for microbial activity, enabling heterotrophic denitrification by facultative anaerobic microbes to occur.
- The occurrence of reduced groundwater in profiles without debris suggests the importance of a) lateral flow of groundwater that was reduced upslope of the sampling location and b) carbon originating from sources other than the woody debris. Carbon residing in the Palaeosol appears to be of lesser importance for the groundwater system's assimilative capacity for nitrate than carbon leached from the topsoil.
- While reduced groundwater was more commonly found at locations with low saturated hydraulic conductivity, the high degree of variation in the limited data available to date necessitates further investigations into the relationship between groundwater redox status and hydraulic properties of the strata.

<u>Effect of denitrification on nitrate nitrogen concentrations at WTWs:</u>

- Circumstantial evidence indicated that the shallow groundwater sampled using WTWs showed at several locations vertical chemistry stratification within the screen range (150 – 600 cm length).
- Vertical stratification of nitrate nitrogen concentrations can arise from variable concentrations in the water recharging from the vadose zone, denitrification occurring below a redox boundary within the depth range of the screen and from the well screen intersecting different lateral flow

paths originating from upslope locations (with different recharge concentrations and/or different redox processes occurring along the flow paths).

- Denitrification is considered responsible for the particularly low nitrate nitrogen concentrations measured in the centre of the Upper Transect (0.49 ± 0.55 mg/L at WR7; 0.63 ± 0.84 mg/L at WR8). Denitrification also appears to have reduced the nitrate nitrogen concentrations at WR16 (and possibly also at WR15, WR12, and WR11) in the Lower Transect.

Effect of well screen length and position on WTW data:

- The thickness of the groundwater zone sampled by the WTWs showed substantial spatial and temporal variation, particularly at the Upper Transect. At the Lower Transect, the thickness of the sampled groundwater column varied only by max. 0.5 m between the well locations and the temporal variation at individual wells was between 1.3 and 1.7 m. In contrast, the water column thickness at individual sampling dates varied between the wells of the Upper Transect by between 0.6 and 3.4 m. Over time, the water column thickness of individual wells varied by between 1.4 and 4.1 m.
- The depth to which a WTW penetrates the saturated zone at a given well location and sampling date will affect the resulting data set whenever and wherever there is a vertical stratification of the groundwater chemistry within the depth range concerned. Accordingly, the data series from well locations WR3, WR16, WR13, and WR11 are considered to be more affected by the length and position of their well screens than the other data series.
- If assessing the effect of recent land use on recharging groundwater is the primary reason for groundwater monitoring, sampling directly at the top of the saturated zone with a short well screen is most appropriate. The thickness of the groundwater column sampled should be standardised across locations and dates to avoid complications arising from possibly existing vertical water chemistry stratification. The well set-up should consequently allow sampling wherever the top of the saturated zone is located at any one point in time. A series of short well screens in fixed depths may be sufficient at sites with little groundwater level variation, but a more flexible set-up appears preferable at sites with a more strongly varying groundwater level.

1 INTRODUCTION

1.1 Background

Land use change over the last 50 years from tussock, shrub-land and indigenous forests to plantation forests and particularly to pastoral farming is considered responsible for early signs of deterioration of the still near-pristine water quality of Lake Taupo. The vadose zone – groundwater – surface water continuum is acknowledged as the conduit for the majority of dissolved contaminants travelling from the land to the lake. This occurs either by direct groundwater discharge through the lake bed or via streams fed by groundwater (Morgenstern, 2007).

As part of a comprehensive, FRST-funded research programme Lincoln Ventures Ltd. established in 2004 a research site in the Lake Taupo catchment. The research carried out there has aimed at reducing the knowledge gap on transport and transformation processes occurring between the bottom of the root zone and the discharge location into surface waters. While soil research has traditionally been very strong in New Zealand and a reasonable body of knowledge has gradually also been built up on groundwater, the connection between these two subsurface components of the hydrological cycle remains poorly understood.

Nitrogen has been the key contaminant studied. As nitrogen transformations are intricately linked to them, carbon species and redox conditions have also been investigated. Vadose zone research at the site has focused on the Spydia research facility (Barkle et al., 2011), while the surrounding Waihora well field was established to investigate the shallow groundwater system that underlies the hillslope and discharges into a wetland at the bottom of the slope (Stenger et al., 2009). The high density of monitoring wells at the Waihora site, combined with intensive monitoring has allowed insight into the spatio-temporal variability of shallow groundwater chemistry at a resolution not possible at conventional monitoring sites.

Shallow groundwater monitoring data collected from 2004 - 2010 at two water table well transects within the Waihora well field are the subject of this report. Given the similarity of lithological and hydrological conditions, these data are also considered relevant for other parts of the Central Plateau, e.g. the Upper Waikato River catchment.

1.2 Scope of work

In contract no. RIG 226, Lincoln Ventures (the Contractor) was contracted by Waikato Regional Council (WRC) to comprehensively review and analyse field data collected from the Waihora well field. The following constitute obligations specified in the contract, which form the objectives of this report:

The Contractor analyses groundwater data it has collected since 2004 under pastoral farming at the Waihora well field in the Tutaeuaua catchment (located in the north-western corner of the Lake Taupo catchment).

In particular the Contractor analyses data in relation to water and nitrogen dynamics produced by monthly sampling of two well transects, consisting of six water table wells (WTWs) in each transect. The data includes analytes of nitrate nitrogen (NO_3-N) and ammonium nitrogen (NH_4-N) for the entire monitoring period (2004 - 2010), and pH, electrical conductivity (EC), dissolved organic carbon (DOC), and dissolved inorganic carbon (DIC) since 2006.
The analysis of the WTWs takes into account that these wells are screened over lengths of between 150 and 600 cm to cover the potential range of seasonally and annually varying water levels and also

that samples consequently represent a bulked sample of that part of the screen that is located below the water table at the time of sampling.

In analyzing the data, the Contractor also takes into account the results of research it has conducted using ten additional multilevel wells (MLWs), which allowed sampling of groundwater from discrete 50 cm depth ranges, and which have shown that strong vertical redox-gradients occur at many locations.

The Contractor provides WRC with a summary report on this water level and groundwater chemistry data and, based on a comparison of results from the WTWs and the MLWs, includes in the report a discussion of the implications of the different well construction types for the interpretation of groundwater quality data.

2 SITE INFORMATION

2.1 Location and land use

The Waihora well field is located north-west of Lake Taupo along Whangamata Road (175°74.997' E, 38°36.863' S) in the headwater area of the Tutaeuaua catchment (Fig.1). The distance between the topographical catchment boundary and the well field is approx. 180 m. The mean annual air temperature during the 2005 – 2010 period was 11.2 ± 0.3 °C. Annual rainfall ranged from 1306 mm to 1645 mm, with a mean of 1467 mm. The mean annual groundwater recharge, estimated as rainfall (R) minus actual evapotranspiration (AET), amounted to 697 ± 257 mm (Appendix I).

Figure 1: Location of the Waihora well field in the Lake Taupo catchment.

For most of the reporting period, the land formed part of Waihora Station owned by Landcorp Farming. Due to Waihora Station's focus on sheep breeding, grazing by beef cattle played only a secondary role. The stocking rate was 8 SU/ha and the browntop pasture produced 5 to 6 tonnes of DM/ha/year. 250 kg/ha Sulphur Super were applied annually, but no N fertiliser. Using the nutrient budgeting model OVERSEER (Ver. 5.4.8, http://www.overseer.org.nz), annual nitrogen leaching of 9 kg/ha/year was estimated by AgResearch (Betteridge and Power, pers. communication, 2010). Since Landcorp Farming sold the farm in 2008, the site has been grazed by calves and heifers belonging to a dairy farming operation (with the milking platform being located just outside the catchment boundary).

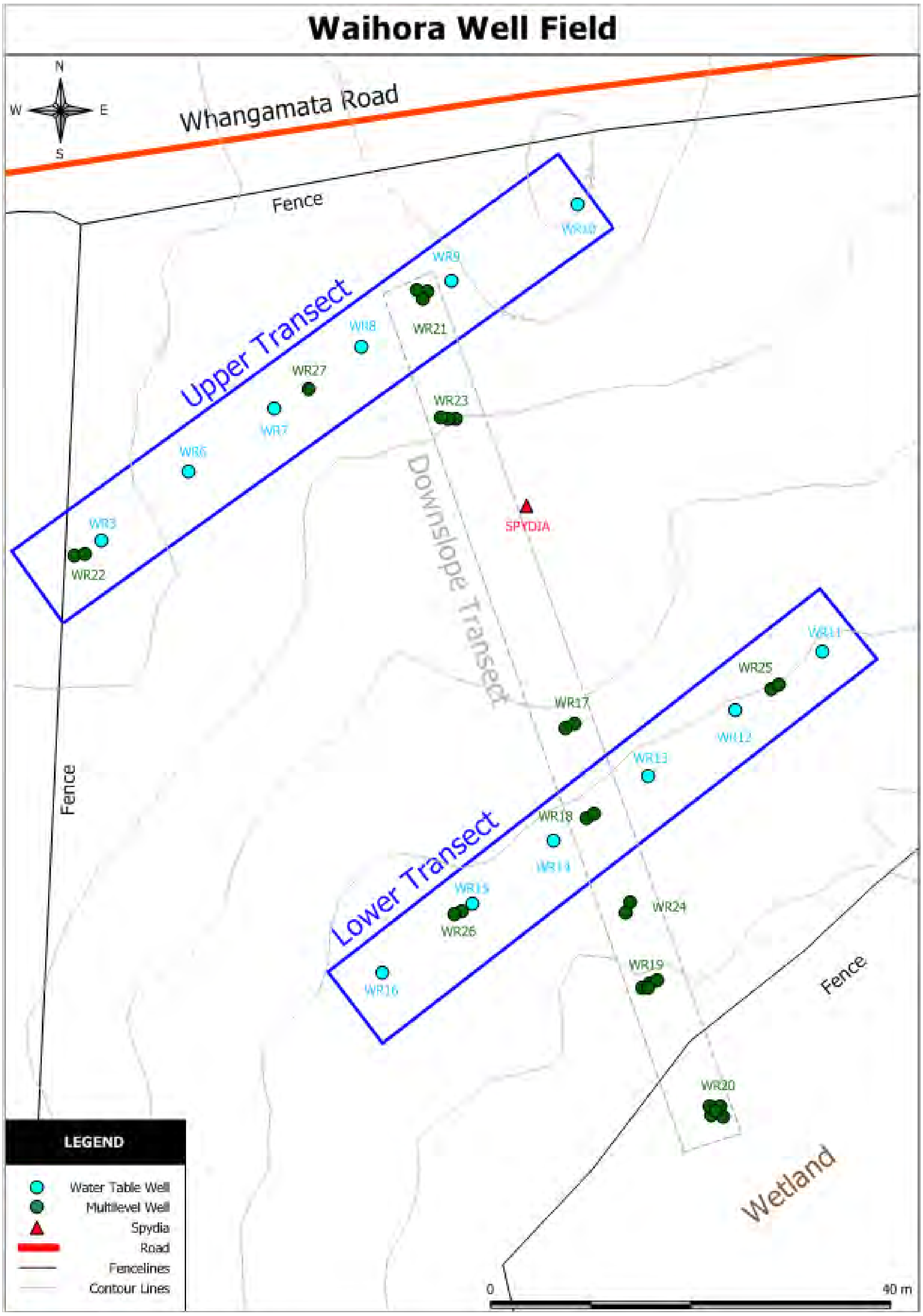


Figure 2: Map of the Waihora well field. Upper and Lower Transects highlighted by blue boxes, Downslope Transect indicated by grey box. WTWs shown as blue dots, MLWs shown as green dots.

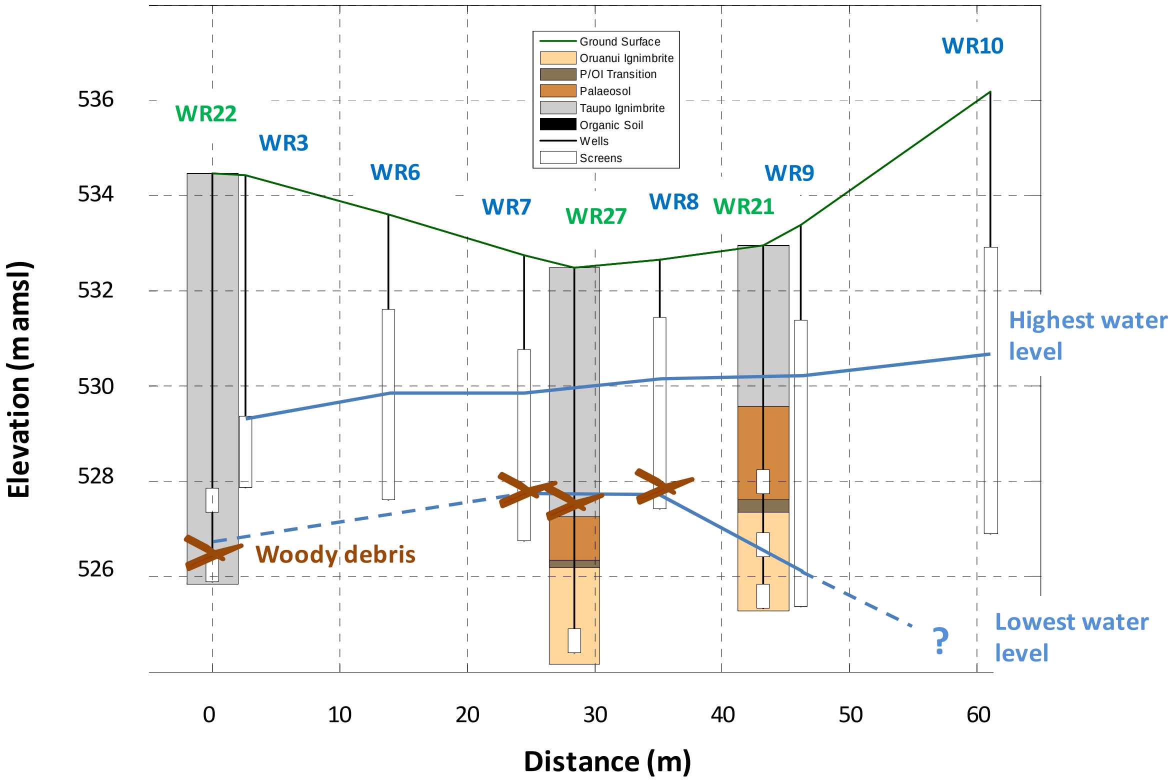
2.2 Well field set-up and stratigraphy

The Waihora well field has a rectangular shape (approx. 65 m * 85 m) and comprises an area of approximately 6000 m^2. It stretches between Whangamata Road on the upper slope and the wetland feeding Tutaeuaua stream at the bottom of the slope (Fig. 2). The elevation ranges from 536 m above mean sea level at a local highpoint near Whangamata Road (well WR10) to 525 m at well WR20 closest to the wetland. The well field consists of a large number of wells of different depths, diameters, and well screen lengths that have been installed successively for particular research purposes. Only the wells relevant for this report are shown in Figure 2.

This report focuses on 12 water table wells (WTWs) that are shown as blue dots in Figure 2. They are located within two well transects that run parallel to each other in a south-west to north-east direction (Fig. 2). The ‘Upper Transect’ is positioned topographically up-gradient of the Spydia vadose zone research facility and the ‘Lower Transect’ is located down-gradient of the Spydia, closer to the wetland to which local shallow groundwater discharges.

Data from selected multilevel wells (MLWs), shown as green dots in Figure 2, are used as supplementary information for the interpretation of WTW results. Most MLWs are located along the ‘Downslope Transect’, but six of them are located within the two parallel transects.

More detailed information on the WTWs and MLWs is given in sections 2.2.2 and 2.2.3, respectively.



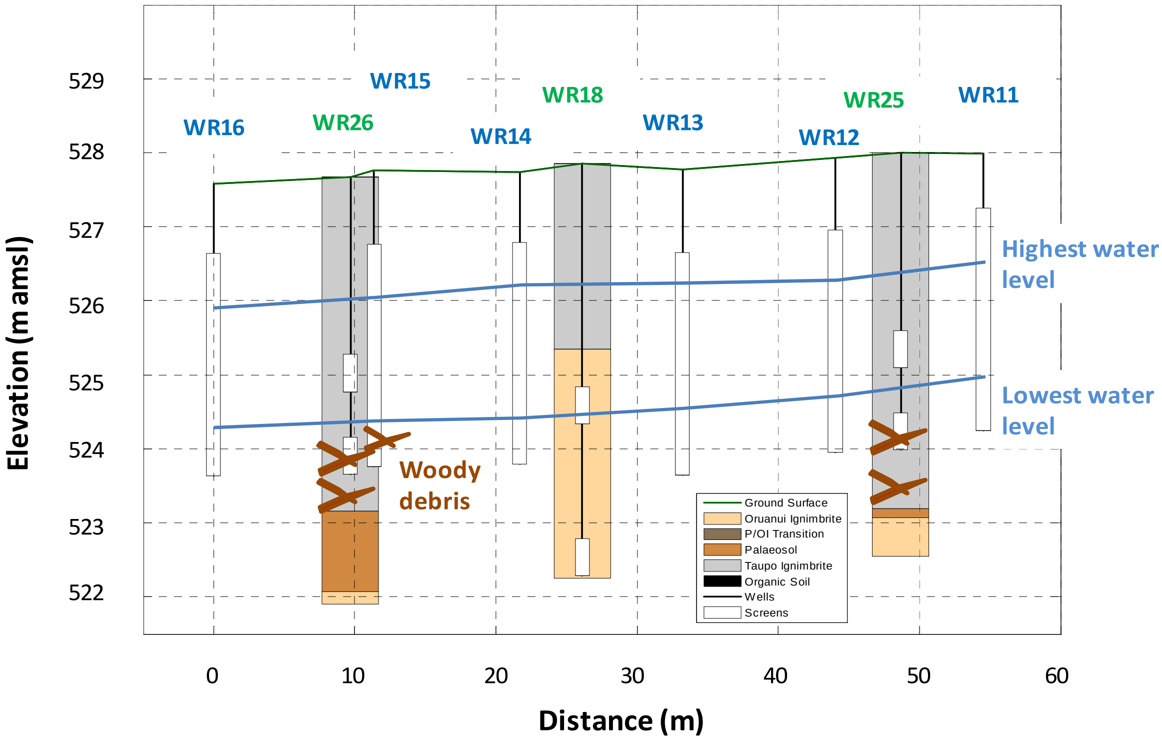


Figure 3: Cross-sections of the Upper and Lower Transects, also showing lithology logged at the MLW locations. Highest and lowest water level measured at each WTW indicated by blue line, dashed where uncertain.

2.2.1 Lithological stratigraphy

The modern soil at the site belongs to the Oruanui loamy sand series within the Podzolic Orthic Pumice Soil subgroup (NZ soil classification) and is a mesic Andic Haplorthod according to U.S. soil taxonomy (Rijkse, 2005). It developed from material deposited during the most recent Taupo eruption approx. 1.8 ka before present (BP) and is found widespread in the Lake Taupo catchment.

Figure 3 shows the lithological stratigraphy as documented when the MLWs were installed in 2007. For the sake of simplicity, the modern Pumice Soil (that constitutes approximately the top 70 cm of the profile) is not differentiated in these cross-sections from its parent material, the unwelded Taupo Ignimbrite (TI). Palaeosol (P) layers of late Pleistocene to early Holocene origin have been found at most boreholes underlying the TI. These 'buried soils' are much finer textured than the sandy TI and are easily recognised by the greasy feel caused by their allophane content. The thickness of the Palaeosols varies between the MLW locations from 13 cm (at WR25) to almost 200 cm (at WR21). No Palaeosol was recorded at WR18 in the middle of the Lower Transect (Fig. 2). Sandy material derived from the Oruanui eruption (26.5 ka BP) underlies the Palaeosols. For a summary of chemical and physical characteristics of these materials refer to Stenger et al. (2006) and Barkle et al. (2011).

A thin relict A horizon at the top of the Palaeosol (Fig. 4) has been found at most locations where the Palaeosol is located below the (long-term) water level (e.g. WR20, WR27, WR26). Equally, woody debris from the vegetation destroyed by the 1.8 ka BP Taupo eruption was also only found in the deepest Taupo Ignimbrite material (and uppermost Palaeosol) where permanently water-saturated conditions prevail (WR20, WR27, WR26, and WR25; see Fig. 3). It is hypothesised that this organic material has been preserved under water-saturation that favours the development of anaerobic conditions, which in turn results in vastly reduced mineralisation rates. In contrast, this material has presumably been completely mineralised during the last 1800 years at those locations where the water level resides below the TI, allowing for aerobic conditions and thus higher mineralisation rates.

Some additional lithological information is available from the earlier WTW installations completed in 2004. Based on this information it appears that the well screens of WR3, WR6, WR7, and WR8 of the Upper Transect are entirely located within the Taupo Ignimbrite (Fig. 3). The profile at WR9 seems to resemble the one described for the adjacent WR21, albeit with a thinner TI layer. The uppermost 2 m at WR10 consist of TI material, but no information is available on the deeper lithology. All WTW screens of the Lower Transect appear to reside in ignimbrite material. It is not known whether a direct transition from TI to OI, as documented for MLW WR18, also occurs at any of the WTWs of the Lower Transect (Fig. 3).

2.2.2 Water table wells (WTWs)

Water Table Wells (WTWs) are defined as 40 mm diameter wells with a relatively long screen (between 150 and 600 cm length) that was set to intersect the water table. Consequently, they allow sampling of an upper groundwater zone of seasonally varying thickness, from the varying location of the top of the saturated zone down to the fixed base of the well (Fig. 3).

A total of twelve WTWs contribute to the two transect datasets considered in this report; six WTWs (WR3, WR6, WR7, WR8, WR9, WR10) are located along the Upper Transect, and six WTWs (WR16, WR15, WR14, WR13, WR12, and WR11) along the Lower Transect (Fig. 3).

2.2.3 Multilevel wells (MLWs)

Each transect also contains three multilevel well clusters (MLWs), each cluster consisting of up to three individual wells screened in different depths (Fig. 3). The MLWs were installed in 2007 to characterise hydrochemical gradients in the shallow groundwater and assess the implications of such gradients on the groundwater's assimilative capacity for nitrate. The MLWs have a diameter of 50 mm, which allowed the use of a submersible pump in a low-flow sampling procedure suitable for on-site measurements of dissolved oxygen, an important indicator of the redox-status of the groundwater (see Box 1, Section 2.3.2).

The MLW clusters allow sampling of discrete depth ranges of 50 cm thickness. The different screen lengths of the WTWs (150 - 600 cm) versus the MLWs (all 50 cm) can be seen in the vertical cross-sections of the two well transects shown in Figure 3.

Multilevel well WR20, located at the lower end of the Downslope Transect (Fig. 2), is used as an example to illustrate the vertical stratigraphy of both lithology and groundwater chemistry encountered at the Waihora well field. As shown in Figure 4, its 5 screens allow establishing groundwater chemistry profiles for the upper 4 – 5 m of the saturated zone. The uppermost screen is located in Taupo Ignimbrite within the water level range, the second screen at the base of the Taupo Ignimbrite where woody debris resides, the third screen in the Palaeosol, and the two deepest screens in the underlying Oruanui Ignimbrite.

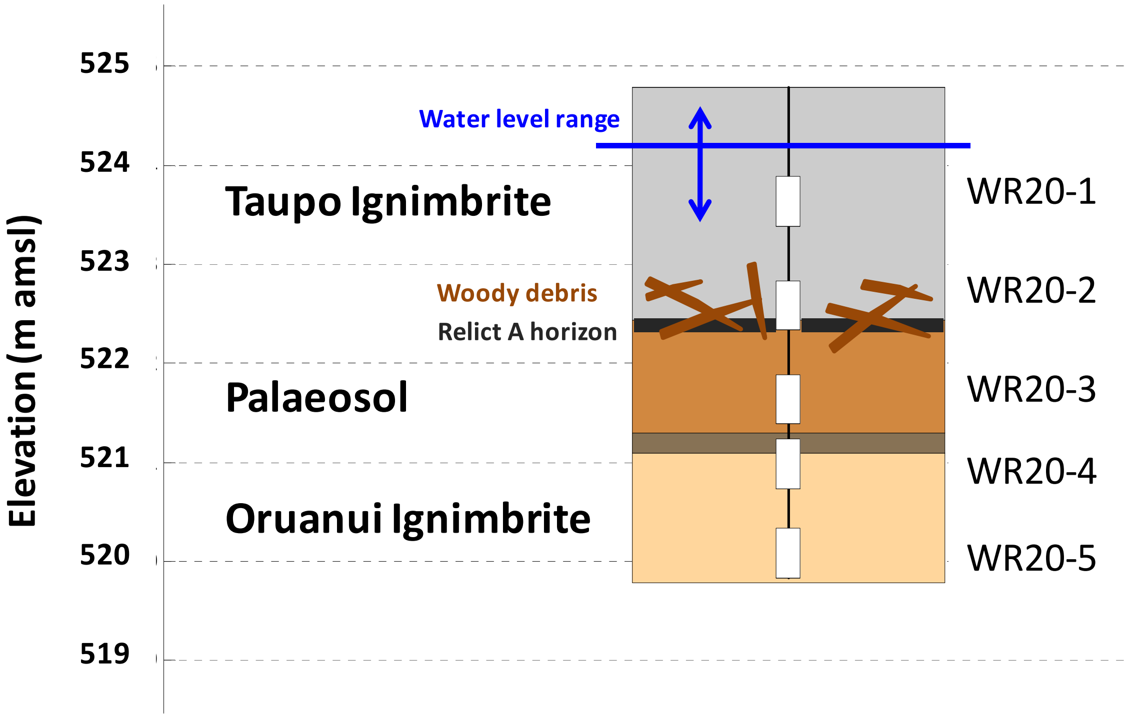


Figure 4: Schematic of lithological stratigraphy and well screen locations at MLW WR20.

2.3 Monitoring programme

Monitoring of groundwater levels and of the chemical composition of shallow groundwater began in 2004 and initially comprised only the WTWs. The monitoring programme was gradually extended as described below.

2.3.1 Groundwater levels

Manual water level measurements using an acoustic sounding tape were undertaken in the WTWs in near-monthly intervals during the period from October 2004 to December 2010. From October 2005, water level dynamics in three wells (WR7, WR9, and WR13) were additionally monitored automatically in 15 min resolution using pressure sensors with integrated data logger (DIVER by Van Essen Instruments and Odyssey by Dataflow Systems Pty Ltd).

2.3.2 Groundwater chemistry

Water Table Wells (WTWs)
Total oxidised nitrogen (NO_x-N), i.e. the sum of nitrate nitrogen (NO_3-N) and nitrite nitrogen (NO_2-N), as well as ammoniacal nitrogen (NH_4-N = NH_4^+-N + NH_3-N) were analysed in near-monthly intervals during the period from November 2004 to December 2010. NO_x-N is in the following used synonymously to NO_3-N, as separate analysis of NO_2-N in our MLWs has shown its concentration to be negligible at our site. MLW NO_2-N concentrations were ≤ 0.002 mg/L in the vast majority of samples and only rarely exceeded 0.01 mg/L.

In May 2006, the monitoring programme was extended to include electrical conductivity (EC), pH, and carbon species. EC and pH were determined by LVL staff using a TPS 90FLMV water quality lab (TPS Pty Ltd, Australia). Carbon analyses comprised Dissolved Total Carbon (DTC), Dissolved Inorganic Carbon (DIC), and Dissolved Organic Carbon (DOC), with the latter being calculated as DOC = DTC – DIC.

All laboratory analyses were carried out by Landcare Research's Environmental Chemistry Laboratory in Palmerston North or Hill Laboratories in Hamilton. Standard detection limits were 0.005 mg L^{-1} for NO_x-N, 0.004 mg L^{-1} for NH_4-N, and 1.0 mg L^{-1} for DOC.

Multilevel Wells (MLWs)
The observation that shallow groundwater in the Toenepi catchment showed a strong vertical redox-stratification (Stenger et al., 2008) led to an extension of the Waihora well field monitoring programme in 2007. A number of multilevel wells (MLWs) with 50 cm long well screens were installed to be able to sample shallow groundwater from discrete depth ranges (as outlined in Section 2.2.3). These MLWs were sampled up to 9 times between August 07 and March 09 with a special focus on redox-sensitive parameters. As described in Box 1, all microbial reactions consuming organic matter are inherently redox reactions, with heterotrophic denitrification (occurring under oxygen-depleted conditions) being the key determinant of a groundwater system's assimilative capacity for nitrate.

Dissolved oxygen (DO), pH and electrical conductivity (EC) were measured on site directly prior to sampling for the laboratory analyses. The field analyses were undertaken using a TPS 90-FLMV field lab (TPS, Springwood, Australia). A well sampling procedure based on the guidelines and stability criteria of the 'National Protocol for State of the Environment Groundwater Sampling in New

Zealand' (Daughney et al., 2006) was used. Additionally to the parameters outlined above, the redox-sensitive parameters dissolved iron (Fe), dissolved manganese (Mn) and sulphate (SO_4) were also determined on these samples (see Eqs. 3 – 5 in Box 1). The samples for the analysis of dissolved Fe and Mn were filtered in the field using a 0.45 µm cellulose acetate syringe-tip filter and preserved with nitric acid. This procedure ensures that dissolved Fe and Mn can be used synonymously with Fe^{2+} and Mn^{2+}, respectively. Detection limits were 0.5 mg/L SO_4, 0.02 mg L^{-1} dissolved Fe and 0.0005 mg L^{-1} dissolved Mn (Hill laboratories, Hamilton).

The concentration of silica in a groundwater sample can be used as a proxy for groundwater age, as it reflects the contact time of the water with silica-bearing minerals in the subsurface environment (see Morgenstern et al., 2011). However, the different solubility of different minerals also affects groundwater silica concentrations. Concentration increases with increasing depth can therefore not exclusively be attributed to increasing water age if the profile encompasses multiple strata of different silica solubility. Silica concentrations (expressed as SiO_2) were determined on selected groundwater samples. Analyses were undertaken by GNS' Wairakei Analytical Laboratory and had a standard detection limit of 0.05 mg/L.

3 GROUNDWATER MONITORING RESULTS

The presentation of the groundwater monitoring results is structured as follows:

Monitoring results from the water table wells (WTWs) are presented in Section 3.1. A figure showing the arithmetic mean (± standard deviation) of each parameter at each WTW in the two transects is presented to provide an initial overview. This figure is complemented by a table containing summary statistics for each individual well, each of the two well transects, and the combined data set. A time series chart demonstrates the temporal dynamics of the parameter concerned. A brief paragraph highlights some of the results in preparation of the discussion in Section 4.

Section 3.2 reports on selected data from the multilevel well clusters (MLWs). Data are presented as plots of vertical chemical profiles. Vertical redox-stratification of groundwater is first demonstrated on the example of WR20, as its 5 well screens allow establishing groundwater chemistry profiles for the upper 4 – 5 m of the saturated zone (TI, P, and OI). Subsequently, data is presented from those MLWs that are located near WTWs within the Upper and Lower Transects.

The discussion of presented data, including the effect of different well types, is given in Section 4.

Box 1: Reduction-oxidation reactions in groundwater

Groundwater chemistry is strongly influenced by microbial activity, since respiration is a redox reaction, involving the transfer of electrons between a substrate and an electron acceptor. Microbial activity itself is determined by the availability of food, such as carbon in organic matter. Potential carbon sources include mobile, dissolved organic carbon recharging from the soil zone and resident organic carbon present in the lithological strata. The latter occurs at the Waihora well field mainly in two forms, as woody debris at the base of the Taupo Ignimbrite stratum and as relict soil organic matter in the underlying Palaeosol ('buried soil') stratum.

Bacteria are able to utilise a variety of electron acceptors in the decomposition of organic matter and these tend to be used in a sequential order based on consideration of their free energy yield and competition for substrate, leading to redox zonation. Under aerobic conditions, oxygen (O_2) is the preferred electron acceptor as using it results in the highest energy yield (Eq. 1). However, if aerobic decomposition becomes limited due to decreasing oxygen levels, bacteria can use a series of alternative electron acceptors (Eqs. 2 -5). Heterotrophic denitrification carried out by facultative anaerobic bacteria is of particular interest for groundwater quality, as this process can remove significant amounts of nitrate from the groundwater and convert it into inert N_2 gas (Eq. 2). In thermodynamic equilibrium, these redox processes would strictly follow the order NO_3^- reduction, closely followed by Mn^{4+} reduction, then Fe^{3+} reduction, and finally almost simultaneously SO_4^{2-} reduction and methane fermentation (Stumm and Morgan, 1996). However, thermodynamic equilibrium does not normally exist in natural systems and the following redox reactions can thus occur concurrently (e.g. Korom, 1992):

(Eq. 1) Aerobic Decomposition

$$CH_2O + O_2 \rightarrow CO_2 + H_2O$$

(Eq. 2) Heterotrophic Denitrification

$$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + H_2CO_3 + 2H_2O$$

(Eq. 3) Manganese (IV) Reduction

$$CH_2O + 2MnO_2 + 3H^+ \rightarrow 2Mn^{2+} + HCO_3^- + 2H_2O$$

(Eq. 4) Ferric Iron (III) Reduction

$$CH_2O + 4Fe(OH)_3 + 7H^+ \rightarrow 4Fe^{2+} + HCO_3^- + 10H_2O$$

(Eq. 5) Sulfate Reduction

$$CH_2O + \tfrac{1}{2} SO_4^{2-} \rightarrow \tfrac{1}{2} HS^- + HCO_3^- + \tfrac{1}{2} H^+$$

(Eq. 6) Methane Fermentation

$$2CH_2O + H_2O \rightarrow CH_4 + HCO_3^- + H^+$$

To provide a simplified classification of groundwater based on its redox status, the terms *'oxidised groundwater'* and *'reduced groundwater'* are frequently used. In this report, any groundwater that contains ≥ 2 mg/L dissolved oxygen (DO) is considered 'oxidised', while groundwater is considered 'reduced' at DO concentrations < 2 mg/L. This threshold was chosen because empirical data from the Waihora well field suggest that heterotrophic denitrification (Eq. 2) can commence once DO concentrations have been decreased to < 2 mg/L.

3.1 Water table wells (WTWs)

3.1.1 Groundwater levels (relative to sea level)

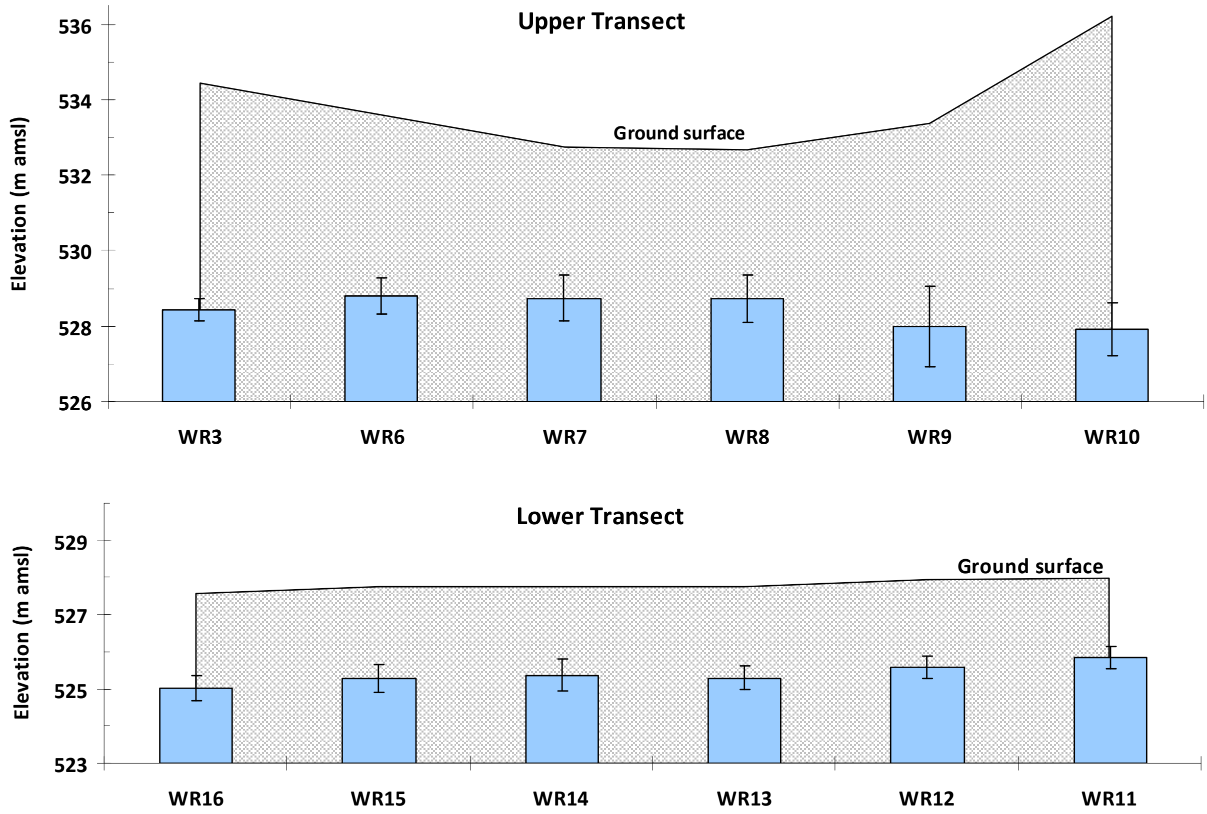


Figure 5: Mean ± standard deviation of the groundwater levels measured in the WTWs (in m above mean sea level).

Table 1: Summary statistics for groundwater levels (in m above mean sea level) [1].

Water level (m above mean sea level), all dates															
	Upper Transect						Lower Transect								
	WR3	WR6	WR7	WR8	WR9	WR10	WR16	WR15	WR14	WR13	WR12	WR11	UT	LT	All
Median	528.37	528.80	528.71	528.66	527.99	527.77	524.97	525.32	525.37	525.28	525.60	525.87	528.50	525.41	526.10
Mean	**528.42**	**528.79**	**528.74**	**528.72**	**527.99**	**527.92**	**525.02**	**525.30**	**525.38**	**525.28**	**525.58**	**525.85**	**528.45**	**525.40**	**526.86**
Stdev	0.30	0.48	0.60	0.62	1.08	0.71	0.34	0.37	0.42	0.32	0.30	0.31	0.77	0.43	1.64
CV	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Min	527.89	527.65	527.63	527.68	526.08	526.94	524.22	524.30	524.40	524.49	524.72	525.02	526.08	524.22	524.22
Max	529.29	529.86	529.86	530.15	530.23	529.84	525.93	526.06	526.20	526.22	526.23	526.59	530.23	526.59	530.23
Range	1.40	2.21	2.23	2.47	4.15	2.90	1.71	1.76	1.79	1.73	1.51	1.57	4.15	2.36	6.01
n	126	162	166	166	166	126	166	166	166	166	165	166	912	995	1907

[1] The following acronyms and abbreviations are used in all tables: Stdev = standard deviation, CV = coefficient of variation (in %), Min = minimum, Max = maximum, n = number of observations, UT = Upper Transect, LT = Lower Transect.

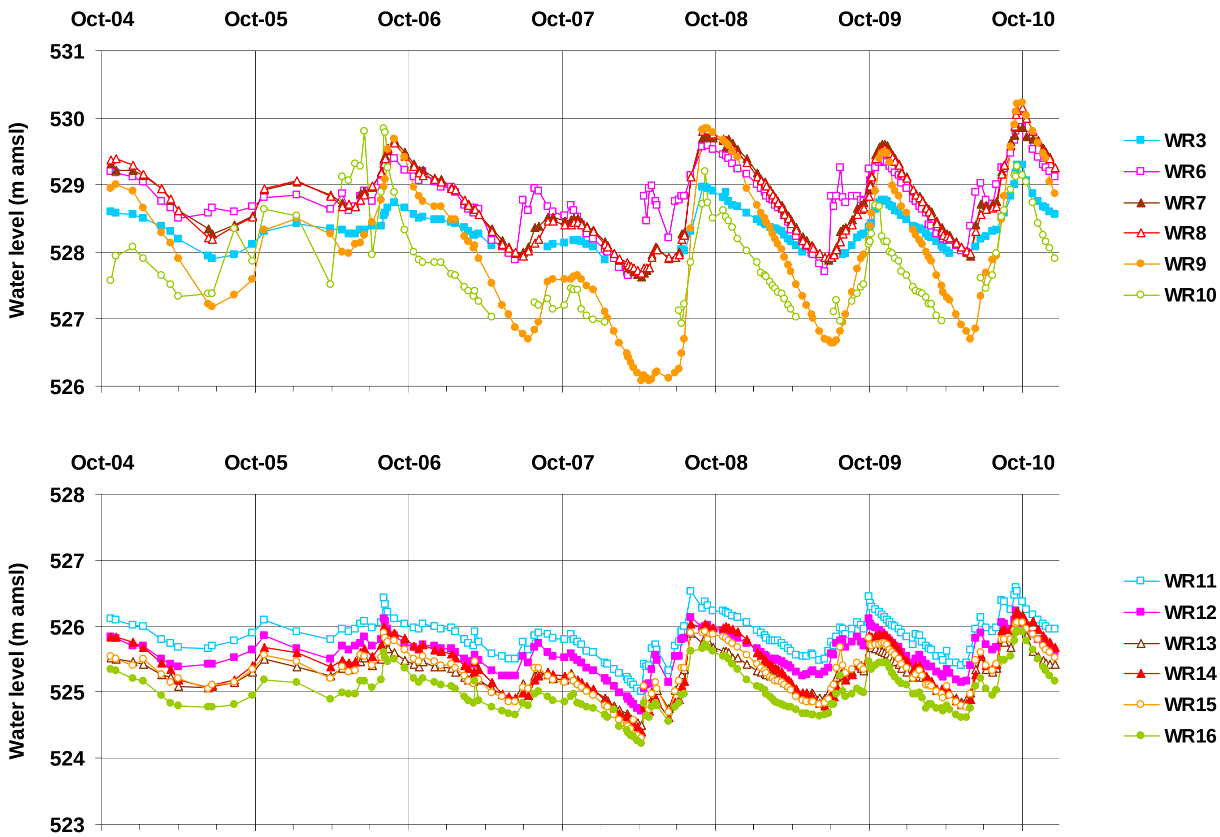


Figure 6: Groundwater level time series for the WTWs (in m above mean sea level).

The mean groundwater level was similar across the centre of the Upper Transect (from WR6 to WR8), however vertical hydraulic gradients sloping down to both ends of the transect are evident (Fig. 5). The hydraulic gradients observed towards the ends of the Upper Transect are the inverse of the topographic gradient. The greatest mean effective gradient of 0.066 m/m was observed between WR8 and WR9. Note that the calculated means for both peripheral wells (528.4 m at WR3, 527.9 m at WR10) are overestimations of real conditions, since these wells periodically dried out, resulting in 24% less observations compared to the other wells in the transect (Tab. 1). A much smaller number of systematic data gaps also occurred at WR6 under particularly dry conditions.

A gentle NE-SW sloping hydraulic gradient is noticeable in the mean groundwater level data from the Lower Transect. The mean hydraulic gradient between WR11 and WR16 was 0.015 m/m. Contrary to the pattern observed in the Upper Transect, the average hydraulic gradient observed within the Lower Transect matches the general topography.

3.1.2 Groundwater levels (relative to ground level)

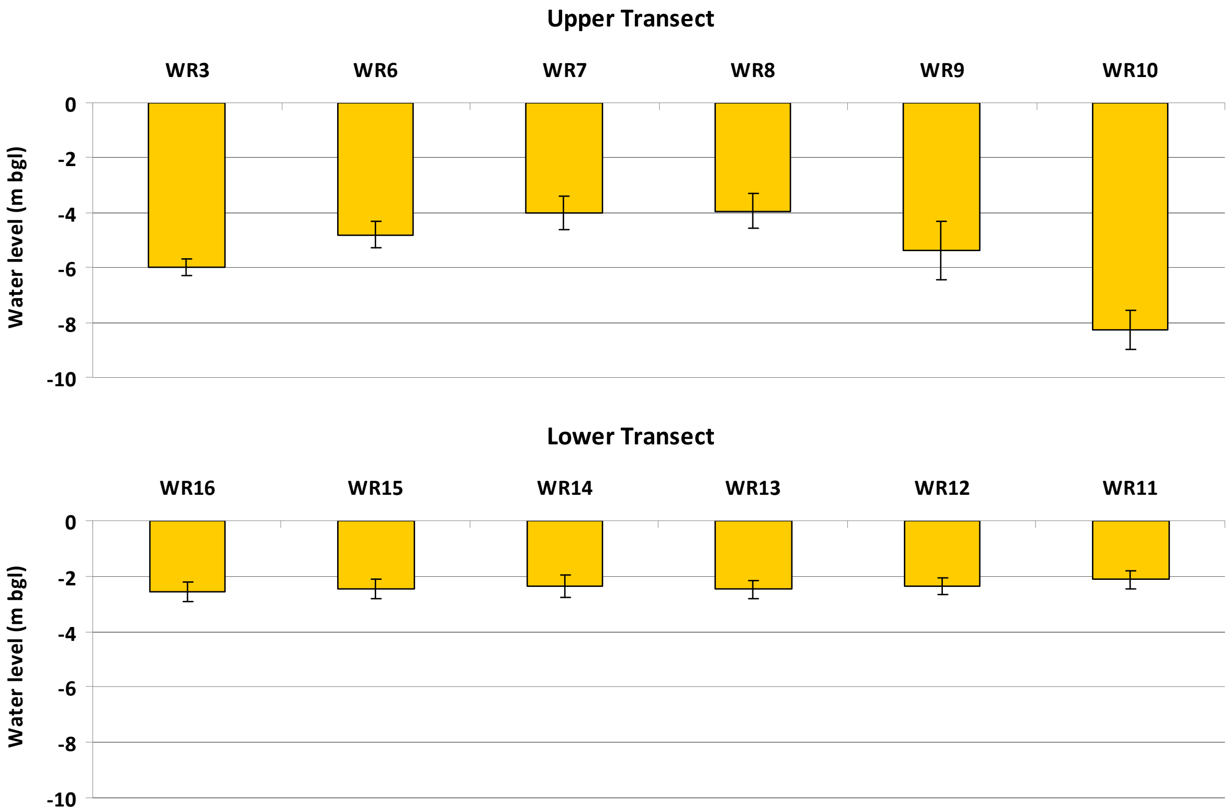


Figure 7: Mean ± standard deviation of the groundwater levels measured at the WTWs (in m below ground level).

Table 2: Summary statistics for groundwater levels (in m below ground level).

Water level (m below ground surface), all dates															
	Upper Transect						**Lower Transect**								
	WR3	**WR6**	**WR7**	**WR8**	**WR9**	**WR10**	**WR16**	**WR15**	**WR14**	**WR13**	**WR12**	**WR11**	**UT**	**LT**	**All**
Median	-6.05	-4.80	-4.04	-4.00	-5.39	-8.42	-2.61	-2.45	-2.37	-2.49	-2.34	-2.12	-4.85	-2.40	-2.96
Mean	**-6.00**	**-4.81**	**-4.00**	**-3.94**	**-5.38**	**-8.27**	**-2.56**	**-2.46**	**-2.36**	**-2.49**	**-2.36**	**-2.14**	**-5.25**	**-2.39**	**-3.76**
Stdev	0.30	0.48	0.60	0.62	1.08	0.71	0.34	0.37	0.42	0.32	0.30	0.31	1.56	0.37	1.81
CV	-5	-10	-15	-16	-20	-9	-13	-15	-18	-13	-13	-15	-30	-16	-48
Min	-6.53	-5.95	-5.11	-4.98	-7.30	-9.25	-3.36	-3.46	-3.34	-3.28	-3.22	-2.97	-9.25	-3.46	-9.25
Max	-5.13	-3.74	-2.88	-2.51	-3.15	-6.35	-1.65	-1.71	-1.54	-1.55	-1.71	-1.40	-2.51	-1.40	-1.40
Range	1.40	2.21	2.23	2.47	4.15	2.90	1.71	1.76	1.80	1.73	1.51	1.57	6.74	2.06	7.85
n	126	162	166	166	166	126	166	166	166	166	165	166	912	995	1907

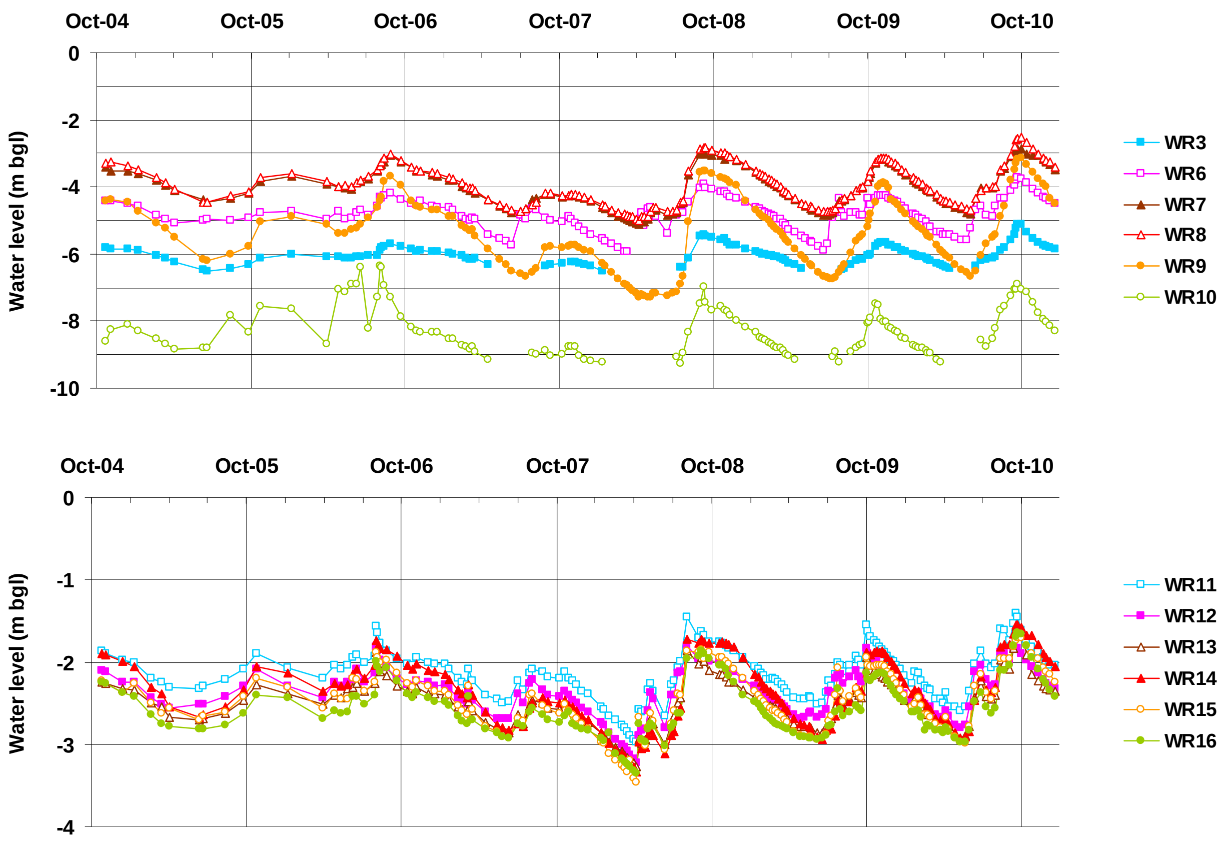
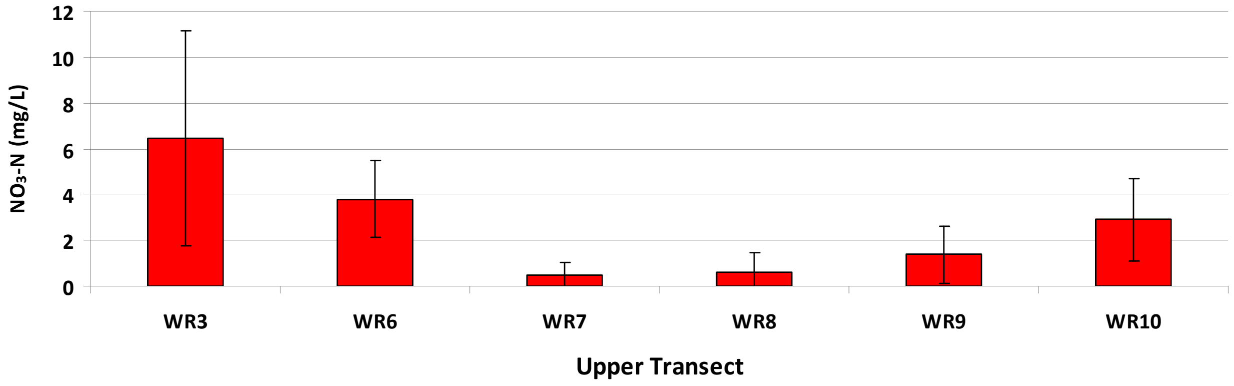


Figure 8: Groundwater levels time series for the WTWs (in m below ground level).

Groundwater levels, when expressed in terms of meters below ground level, are effectively a measure of the thickness of the vadose zone. The average vadose zone thickness across the middle of the Upper Transect is 4.0 m. It is significantly greater at both ends of the transect (6.0 m at WR3, 8.3 m at WR10), as a combined effect of surface topographic differences and hydraulic gradients, as noted in Section 3.1.1. As noted previously, the latter values are underestimations due to data gaps having occurred at these sites under particularly dry conditions. Groundwater levels were much more uniform and shallower at the Lower Transect; means ranging from 2.1 m (WR11 at the NE end) to 2.6 m (WR16 at the SW end).

The amplitude of seasonal groundwater fluctuations at individual well sites was substantially smaller at the Lower Transect wells (1.5 to 1.8 m) as compared to the Upper Transect wells, but there was also a substantial variation amongst the wells of the Upper Transect (Tab. 2). In spite of missing data under particularly dry conditions, it would appear that the water level varied by less than 2 m at WR3, but it varied by 4.15 m at WR9.

3.1.3 Nitrate nitrogen (NO_3-N)



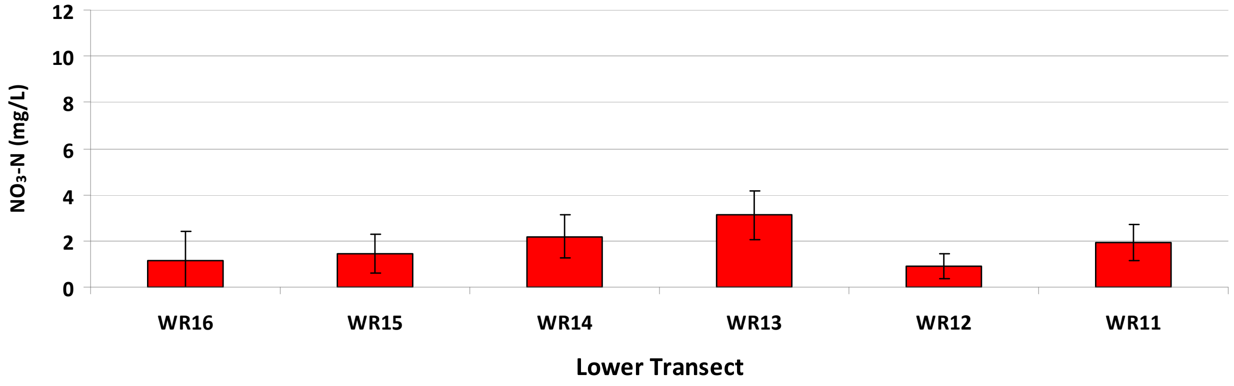


Figure 9: Mean ± standard deviation of nitrate nitrogen at the WTWs (in mg/L).

Table 3: Summary statistics for nitrate nitrogen (in mg/L).

Nitrate nitrogen (NO_3-N), (mg/L)															
	Upper Transect						Lower Transect								
	WR3	WR6	WR7	WR8	WR9	WR10	WR16	WR15	WR14	WR13	WR12	WR11	UT	LT	All
Median	4.94	3.68	0.26	0.21	1.16	2.32	0.76	1.32	1.90	3.16	0.82	2.09	1.30	1.64	1.53
Mean	**6.44**	**3.79**	**0.49**	**0.63**	**1.37**	**2.91**	**1.16**	**1.46**	**2.18**	**3.11**	**0.91**	**1.91**	**2.38**	**1.79**	**2.07**
Stdev	4.70	1.68	0.55	0.84	1.24	1.79	1.24	0.85	0.93	1.06	0.53	0.78	2.90	1.17	2.18
CV	73	44	113	133	90	61	107	58	43	34	59	41	121	66	105
Min	1.05	0.02	0.00	0.00	0.11	0.00	0.00	0.25	1.01	0.66	0.00	0.05	0.00	0.00	0.00
Max	18.30	9.65	2.28	3.35	6.81	6.31	6.50	4.14	5.44	4.84	2.63	3.15	18.30	6.50	18.30
Range	17.25	9.63	2.28	3.35	6.70	6.31	6.50	3.89	4.43	4.18	2.63	3.10	18.30	6.50	18.30
n	44	56	60	60	60	42	60	60	60	60	60	60	322	360	682

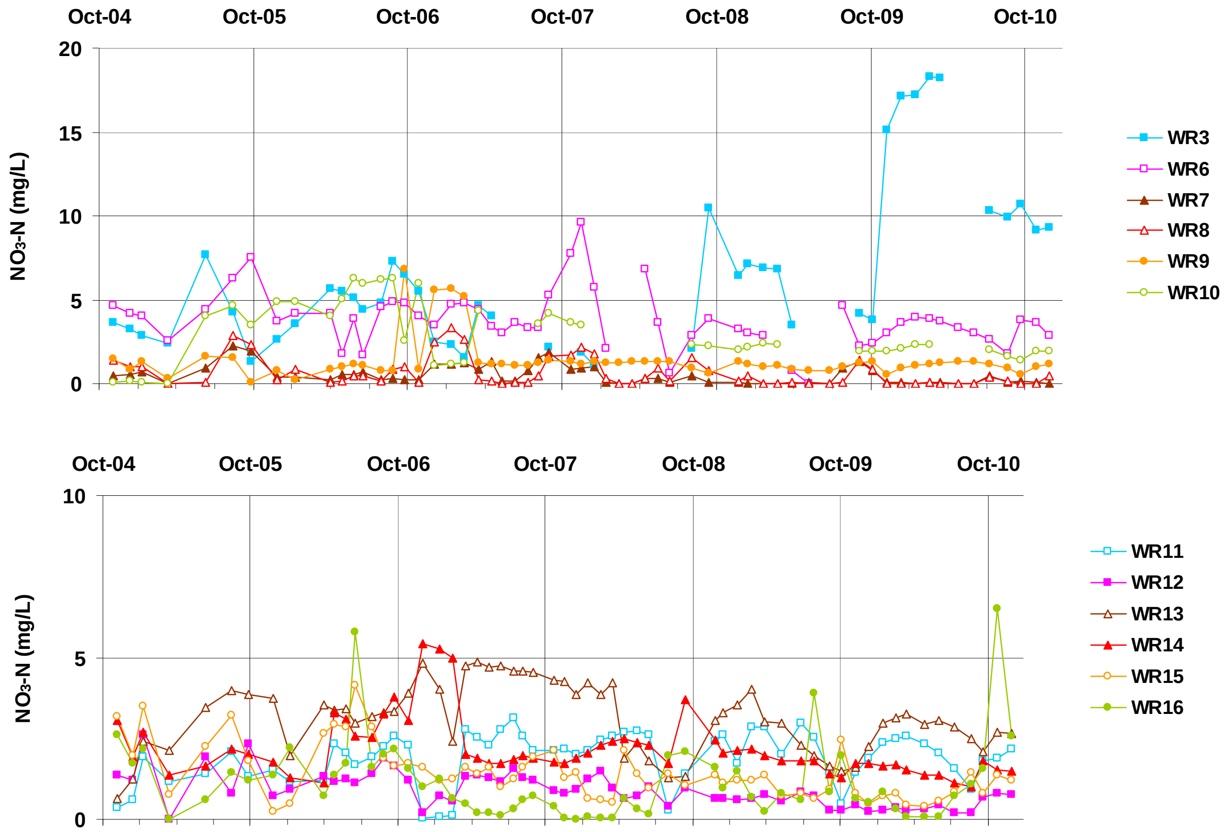


Figure 10: Nitrate nitrogen time series for the WTWs (in mg/L).

The overall mean NO_3-N concentration of all 682 groundwater samples analysed in near-monthly intervals between 2004 and 2010 was 2.07 mg/L; the median was lower at 1.53 mg/L. NO_3-N concentrations were on average higher and more variable at the Upper Transect (2.38 ± 2.90 mg/L) than at the Lower Transect (1.79 ± 1.17 mg/L).

In the Upper Transect nitrate concentrations were on average higher at the periphery of the transect, whereas at the Lower Transect, higher concentrations occurred in the centre.

Since wells WR3 and WR10 (and to a much lesser extent WR6) were periodically dry, they often could not be sampled between late summer and early winter. These data gaps result in slight overestimations of the mean concentrations reported for WR3 and WR10 (Tab. 3), as weak positive correlations between water level and NO_3-N concentrations exist at these two wells (see Section 4 and Appendix II).

There were marked differences between the wells in the temporal dynamics of NO_3-N concentrations. Using the combined rankings of standard deviation and observed ranges as criteria, wells WR3, WR6, and WR10 had the most variable concentrations over time, while wells WR7, WR11 and WR12 showed the least temporal variation (Fig. 10).

The data series do not indicate any consistent long-term trend in the nitrate concentrations for the six years of monitoring.

3.1.4 Ammoniacal nitrogen (NH_4-N)

Figure 11: Mean ± standard deviation of ammoniacal nitrogen at the WTWs (in mg/L).

Table 4: Summary statistics for ammoniacal nitrogen (in mg/L).

Ammoniacal nitrogen (NH4-N), (mg/L)															
	Upper Transect						**Lower Transect**								
	WR3	**WR6**	**WR7**	**WR8**	**WR9**	**WR10**	**WR16**	**WR15**	**WR14**	**WR13**	**WR12**	**WR11**	**UT**	**LT**	**All**
Median	0.07	0.18	0.14	0.09	0.02	0.04	0.04	0.02	0.02	0.02	0.02	0.04	0.07	0.02	0.03
Mean	**0.34**	**0.35**	**0.13**	**0.11**	**0.03**	**0.05**	**0.08**	**0.03**	**0.02**	**0.07**	**0.04**	**0.06**	**0.17**	**0.05**	**0.10**
Stdev	0.90	0.54	0.09	0.10	0.04	0.04	0.13	0.03	0.02	0.24	0.07	0.09	0.42	0.12	0.31
CV	265	151	71	87	105	81	163	112	104	352	174	132	254	246	295
Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Max	5.13	2.80	0.34	0.50	0.16	0.14	0.64	0.15	0.11	1.87	0.40	0.42	5.13	1.87	5.13
Range	5.13	2.80	0.33	0.50	0.16	0.14	0.64	0.15	0.11	1.87	0.39	0.42	5.13	1.87	5.13
n	44	56	60	60	60	42	60	60	60	60	60	60	322	360	682

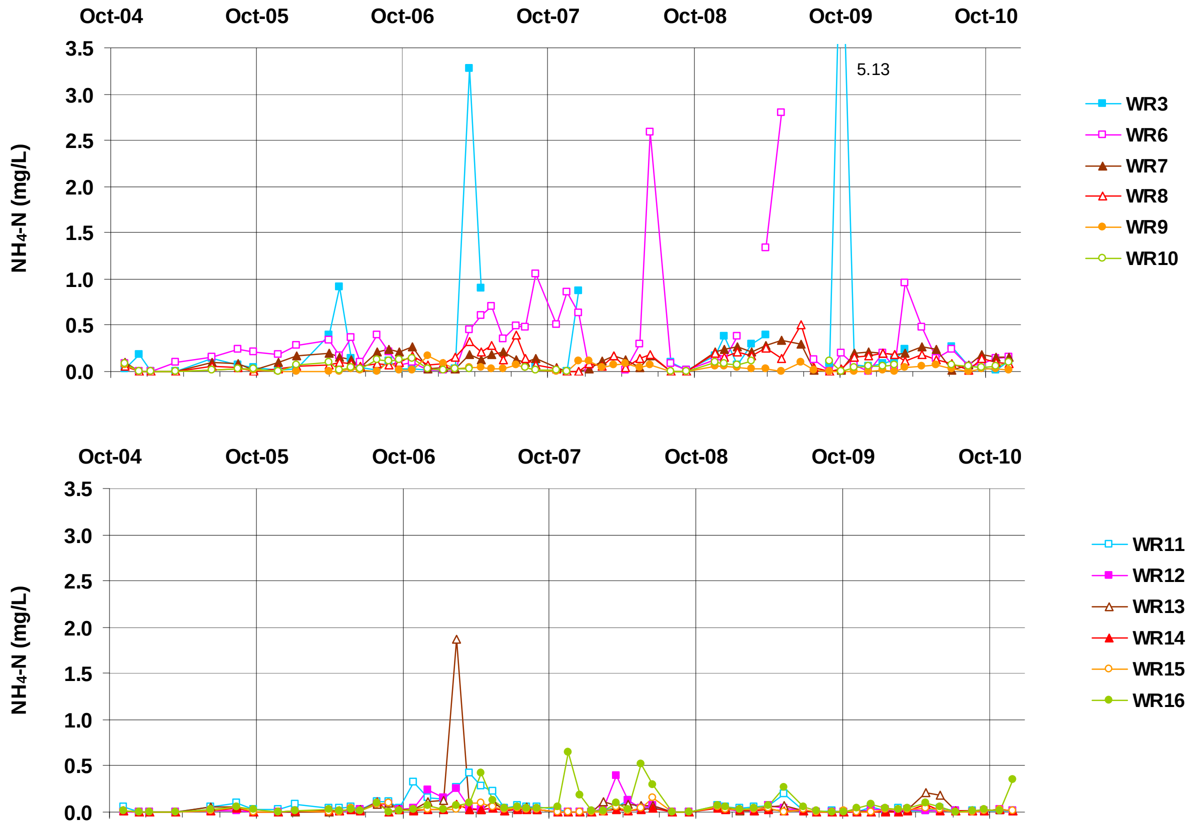


Figure 12: Ammoniacal nitrogen time series for the WTWs (in mg/L).

NH_4-N concentrations in shallow groundwater were substantially lower than NO_3-N concentrations. The mean NH_4-N concentration of 0.10 mg/L equates to just 5% of the mean NO_3-N concentration; the difference between median values is even greater (Tab. 4). The general spatial distribution of NH_4-N concentrations is similar to that observed for NO_3-N, i.e. higher and more variable concentrations along the Upper Transect (0.17 ± 0.42 mg/L) relative to the Lower Transect (0.05 ± 0.12 mg/L).

A prolonged period of enhanced NH_4-N concentrations was observed at WR6, lasting much of 2007. Aside from this period, NH_4-N concentrations above 0.5 mg/L have been confined to short-lived peaks that occurred at WR3, WR16 and WR13 (Fig. 12). Only the NH_4-N peak observed at WR3 in October 2009 (NH_4-N levels topped 5.13 mg/L) corroborates with any NO_3-N peaks.

3.1.5 pH

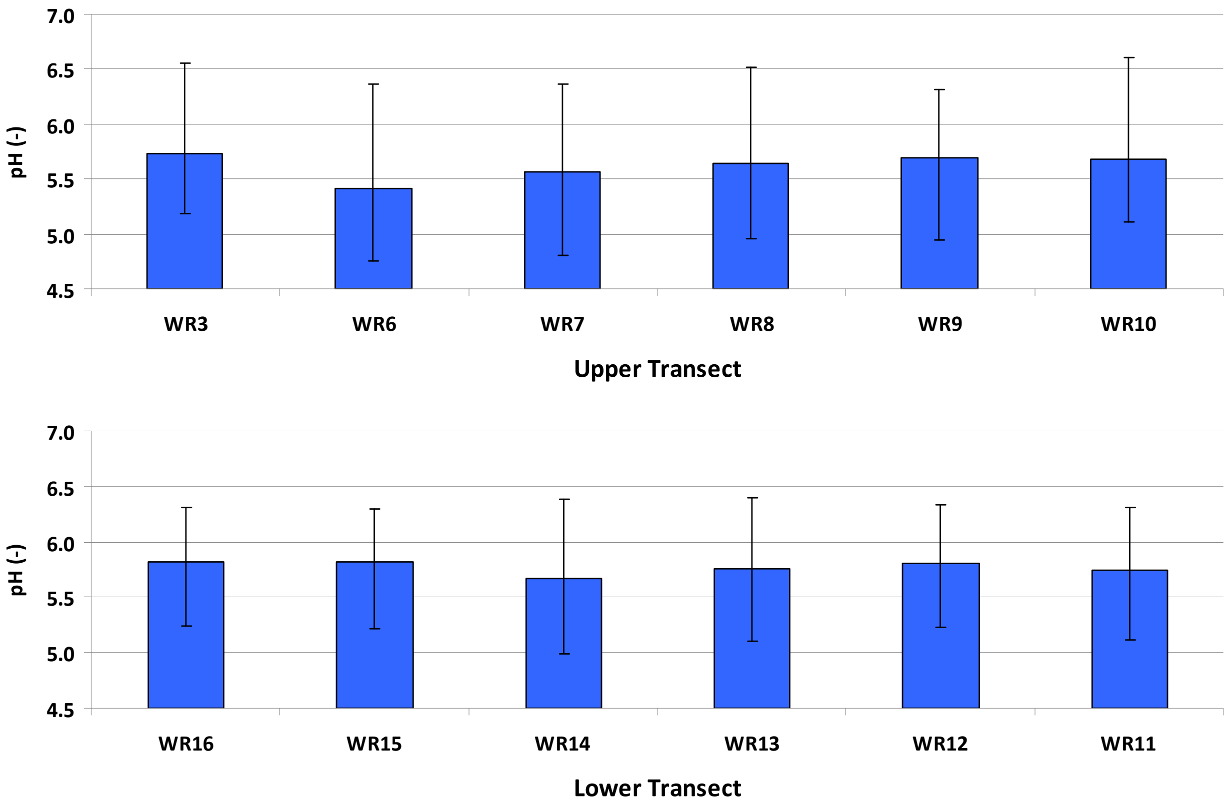


Figure 13: Mean, minimum, and maximum of pH values at the WTWs.

Table 5: Summary statistics for pH[2]*.*

pH (-)	Upper Transect						Lower Transect								
	WR3	WR6	WR7	WR8	WR9	WR10	WR16	WR15	WR14	WR13	WR12	WR11	UT	LT	All
Median	5.9	5.7	5.7	5.9	5.9	5.9	5.9	5.9	5.9	5.9	6.0	6.0	5.8	5.9	5.9
Mean	**5.7**	**5.4**	**5.6**	**5.6**	**5.7**	**5.7**	**5.7**	**5.8**	**5.8**	**5.7**	**5.8**	**5.8**	**5.8**	**5.9**	**5.8**
Stdev															
CV															
Min	5.2	4.8	4.8	5.0	5.0	5.1	5.1	5.2	5.1	5.0	5.2	5.2	4.8	5.0	4.8
Max	6.6	6.4	6.4	6.5	6.3	6.6	6.3	6.3	6.4	6.4	6.3	6.3	6.6	6.6	6.6
Range	1.4	1.6	1.6	1.6	1.4	1.5	1.2	1.1	1.3	1.4	1.1	1.1	1.9	1.6	1.9
n	33	47	50	50	50	30	48	50	50	50	49	50	260	297	557

[2] Due to the logarithmic nature of pH values, medians and means were calculated based on the H^+ ion activity and then back-transformed into pH values.

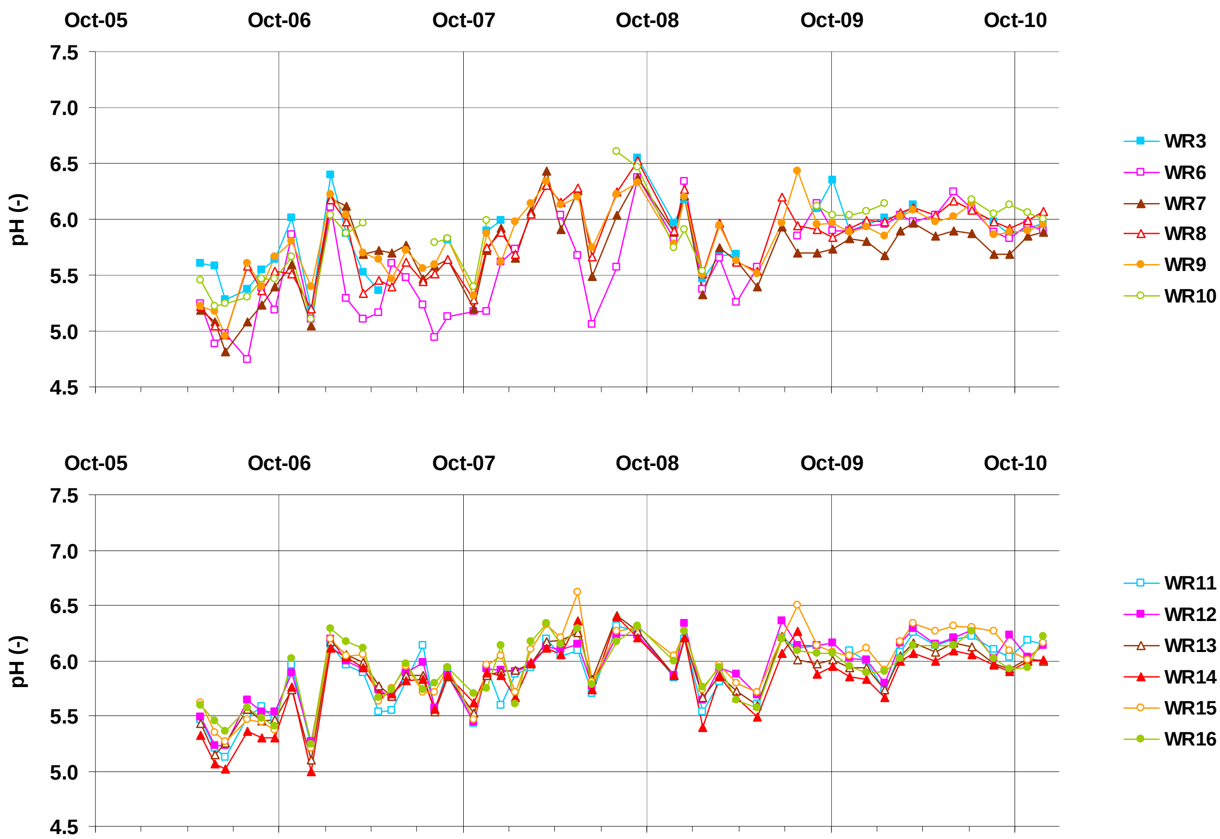


Figure 14: pH value time series for the WTWs.

pH levels in the shallow groundwater varied between 4.8 and 6.6; with an overall mean of 5.8. The mean pH was tentatively lower at the Upper Transect (pH 5.8) than at the Lower Transect (pH 5.9). Variability between wells was slightly higher at the Upper Transect.

Contrary to other monitored variables, there is a clear trend of increasing pH, particularly in the early stages of the monitoring period (2006 – 2007).

3.1.6 Electrical Conductivity (EC)

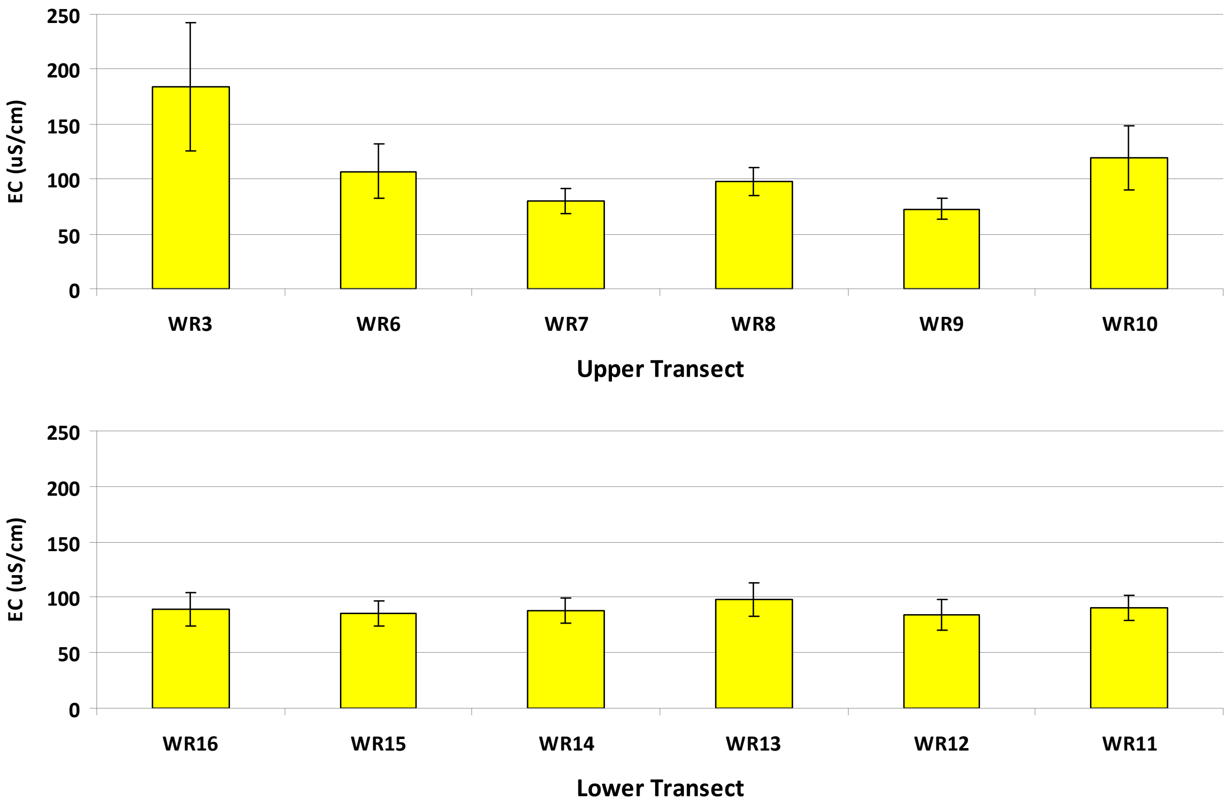


Figure 15: Mean ± standard deviation of the electrical conductivity at the WTWs (in µS/cm).

Table 6: Summary statistics for electrical conductivity (in µS/cm).

Electrical Conductivity (EC), (uS/cm)															
	Upper Transect						Lower Transect								
	WR3	WR6	WR7	WR8	WR9	WR10	WR16	WR15	WR14	WR13	WR12	WR11	UT	LT	All
Median	175	108	82	97	72	121	88	85	90	99	86	92	91	91	91
Mean	**184**	**107**	**80**	**98**	**73**	**120**	**90**	**86**	**88**	**98**	**84**	**91**	**105**	**89**	**97**
Stdev	58	25	11	13	9	29	15	12	11	15	14	12	43	14	32
CV	32	23	14	13	12	24	17	14	13	15	17	13	41	15	33
Min	92	63	56	67	56	80	38	54	43	44	54	58	56	38	38
Max	388	177	112	125	90	172	142	102	109	120	107	112	388	142	388
Range	297	114	56	58	34	92	104	48	67	76	53	55	332	104	350
n	34	47	50	50	50	30	50	49	50	50	50	48	261	297	558

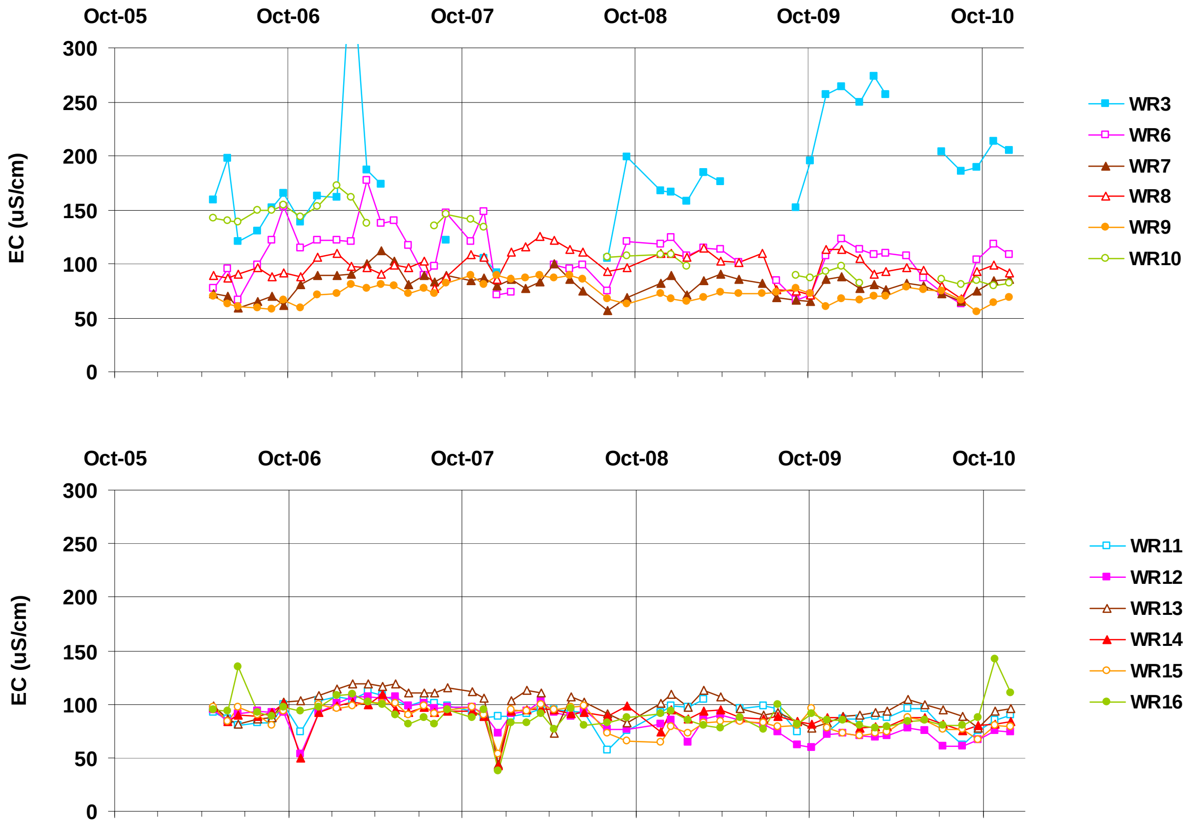
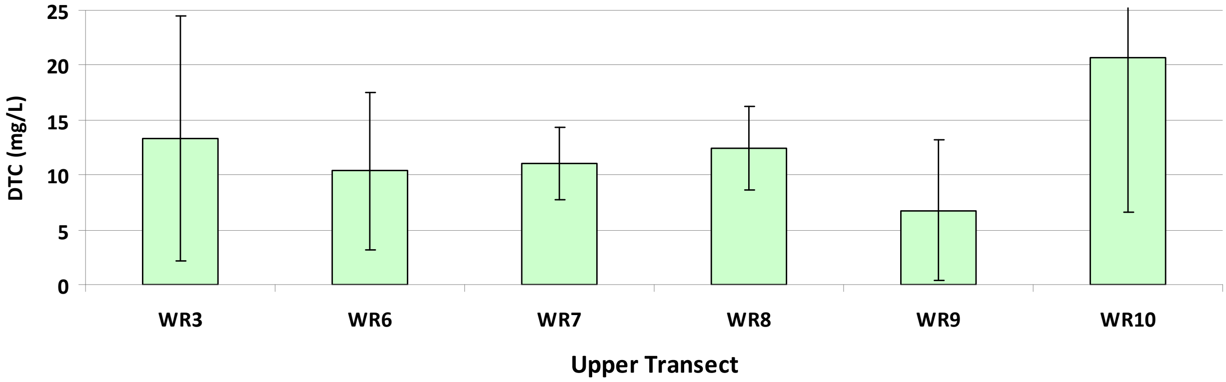


Figure 16: Electrical conductivity time series for the WTWs (in µS/cm).

Compared to most other measured parameters, the measured electrical conductivities showed little spatial and temporal variation. Coefficients of variation were a maximum of 17% for all wells of the Lower Transect and WR7, WR8, and WR9 of the Upper Transect, all of which had a mean conductivity between 84 and 98 µS/cm. Only wells WR6, WR10, and particularly WR3 had higher and more variable electrical conductivities, reflecting greater and more variable total ion content.

3.1.7 Dissolved Total Carbon (DTC)



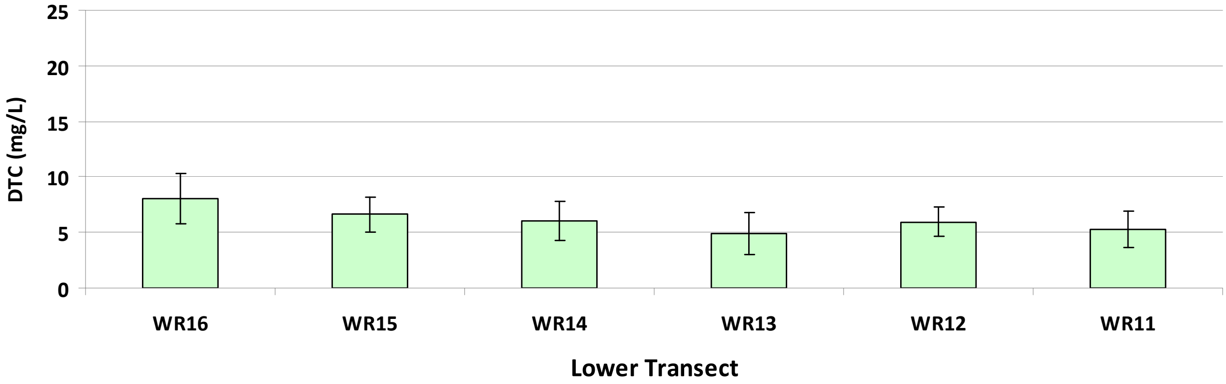


Figure 17: Mean ± standard deviation of dissolved total carbon at the WTWs (in mg/L).

Table 7: Summary statistics for dissolved total carbon (in mg/L).

Dissolved Total Carbon (DTC), (mg/L)															
	Upper Transect						Lower Transect								
	WR3	**WR6**	**WR7**	**WR8**	**WR9**	**WR10**	**WR16**	**WR15**	**WR14**	**WR13**	**WR12**	**WR11**	**UT**	**LT**	**All**
Median	10.0	8.5	11.0	12.0	6.0	16.0	8.0	6.5	6.0	4.5	6.0	5.0	10.0	6.0	7.0
Mean	**13.3**	**10.4**	**11.0**	**12.4**	**6.8**	**20.6**	**8.1**	**6.6**	**6.1**	**4.9**	**5.9**	**5.3**	**11.8**	**6.2**	**8.8**
Stdev	11.1	7.2	3.3	3.8	6.4	14.1	2.2	1.6	1.7	1.9	1.3	1.6	8.7	2.0	6.7
CV	83	69	30	30	95	68	28	24	29	38	22	31	74	33	77
Min	6.0	3.0	5.0	5.0	3.0	12.0	4.0	4.0	4.0	3.0	4.0	3.0	3.0	3.0	3.0
Max	52.0	49.0	21.0	23.0	49.0	74.0	12.0	10.0	11.0	12.0	9.0	10.0	74.0	12.0	74.0
Range	46.0	46.0	16.0	18.0	46.0	62.0	8.0	6.0	7.0	9.0	5.0	7.0	71.0	9.0	71.0
n	34	46	50	50	50	32	50	50	50	50	50	50	262	300	562

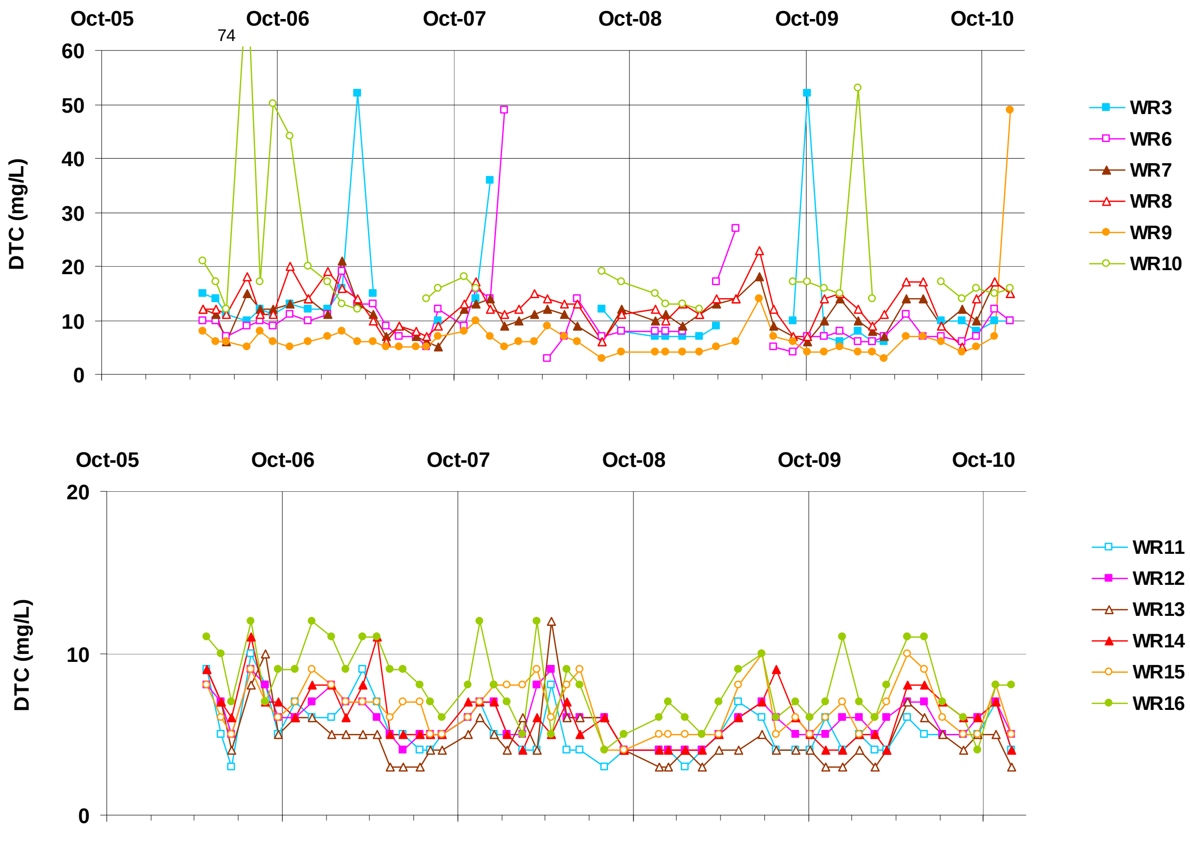


Figure 18: Dissolved total carbon time series for the WTWs (in mg/L). Note the difference in vertical scale of charts.

The overall mean DTC concentration of all 562 analysed groundwater samples was 8.8 mg/L. The mean DTC concentration of the Upper Transect samples (11.8 mg/L) was almost twice as high as that of the Lower Transect samples (6.2 mg/L). The higher mean DTC concentration (and the greater variability) at the Upper Transect are partly due to a number of very high concentration peaks observed at the peripheral wells WR3, WR6, WR9 and WR10. However, disregarding all concentration peaks > 25 mg/L, the mean DTC concentration at the Upper Transect still remains approx. 70% higher than that at the Lower Transect.

3.1.8 Dissolved Inorganic Carbon (DIC)

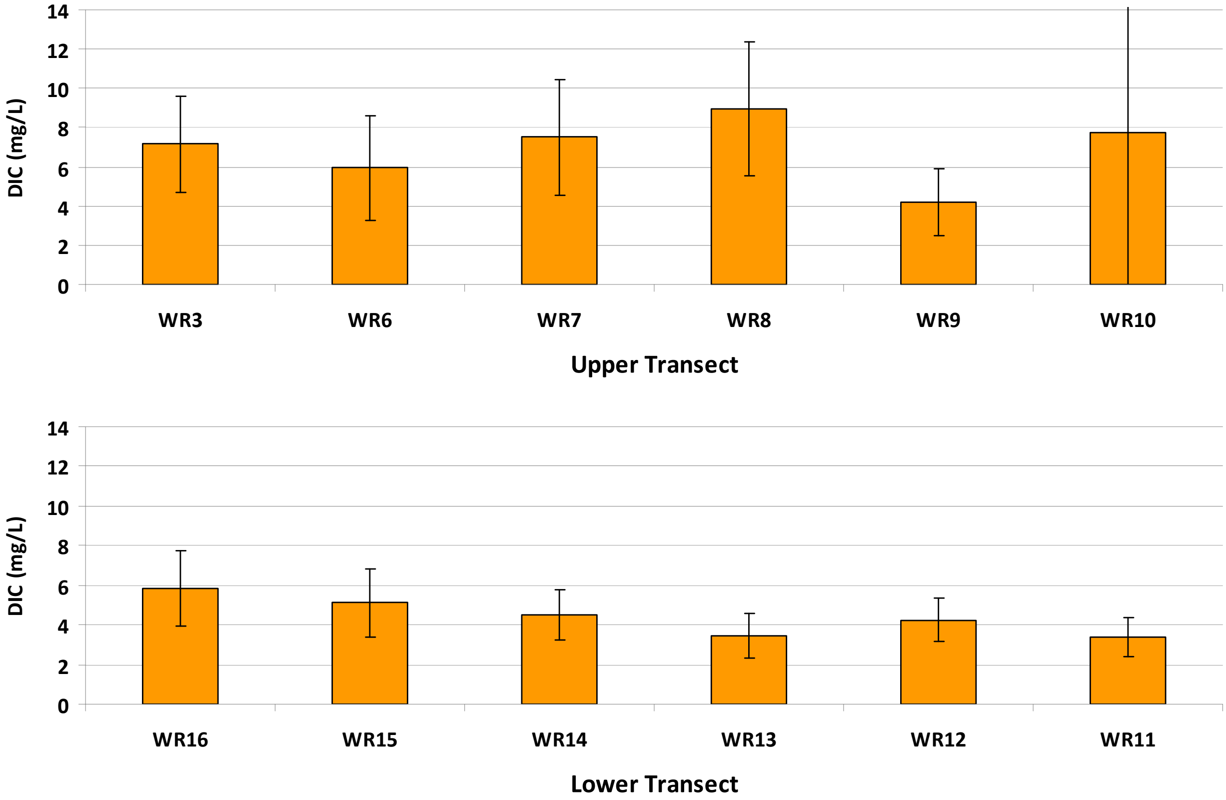


Figure 19: Mean ± standard deviation of dissolved inorganic carbon at the WTWs (in mg/L).

Table 8: Summary statistics for dissolved inorganic carbon (in mg/L).

Dissolved Inorganic Carbon (DIC), (mg/L)															
	Upper Transect						Lower Transect								
	WR3	WR6	WR7	WR8	WR9	WR10	WR16	WR15	WR14	WR13	WR12	WR11	UT	LT	All
Median	7.5	5.0	8.0	9.0	4.0	5.0	6.0	5.0	4.0	3.0	4.0	3.0	6.0	4.0	5.0
Mean	**7.1**	**5.9**	**7.5**	**9.0**	**4.2**	**7.7**	**5.9**	**5.1**	**4.5**	**3.4**	**4.2**	**3.4**	**6.9**	**4.4**	**5.6**
Stdev	2.5	2.7	3.0	3.4	1.7	8.9	1.9	1.7	1.3	1.1	1.1	1.0	4.3	1.6	3.4
CV	34	45	39	38	40	116	33	33	29	32	26	29	63	37	61
Min	2.0	2.0	3.0	3.0	1.0	4.0	2.0	1.0	1.0	1.0	1.0	2.0	1.0	1.0	1.0
Max	12.0	13.0	15.0	20.0	11.0	44.0	10.0	9.0	7.0	6.0	7.0	6.0	44.0	10.0	44.0
Range	10.0	11.0	12.0	17.0	10.0	40.0	8.0	8.0	6.0	5.0	6.0	4.0	43.0	9.0	43.0
n	34	46	50	50	50	32	50	50	50	50	50	50	262	300	562

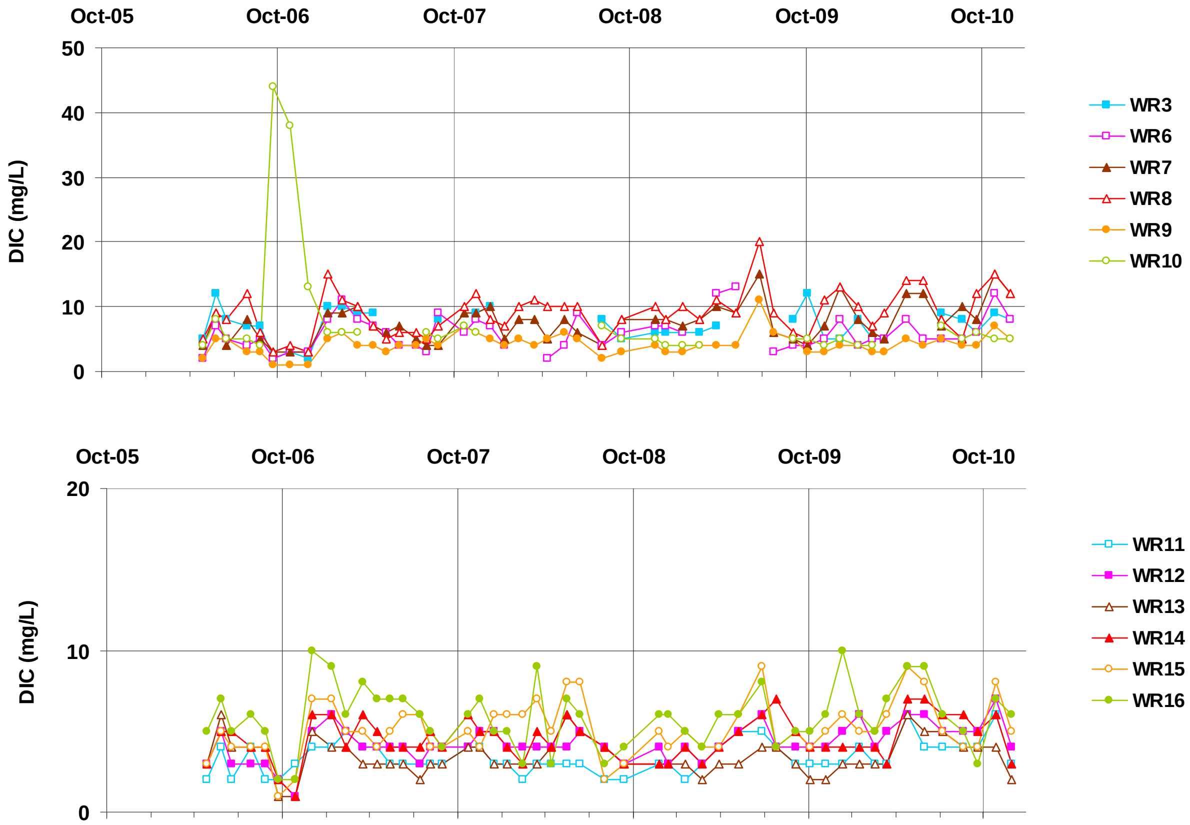


Figure 20: Dissolved inorganic carbon time series for the WTWs (in mg/L). Note the difference in vertical scale of charts.

The overall mean DIC concentration was 5.0 mg/L. The mean DIC concentration at the Upper Transect (6.9 mg/L) was approx. 60% higher than at the Lower Transect (4.4 mg/L). The smaller difference between the transects in DIC as compared to DTC is partly due to distinct concentration peaks that occurred more frequently in the DTC dataset from the Upper Transect than in the corresponding DIC dataset.

3.1.9 Dissolved Organic Carbon (DOC)

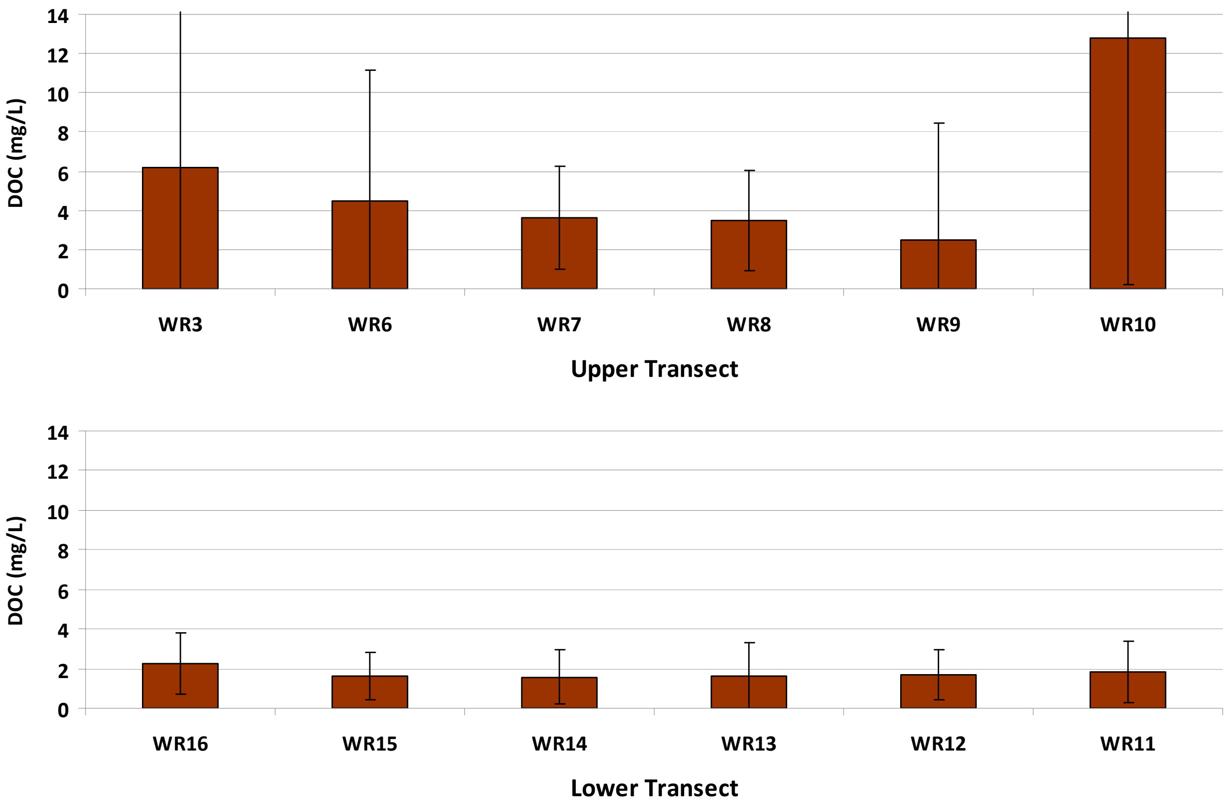
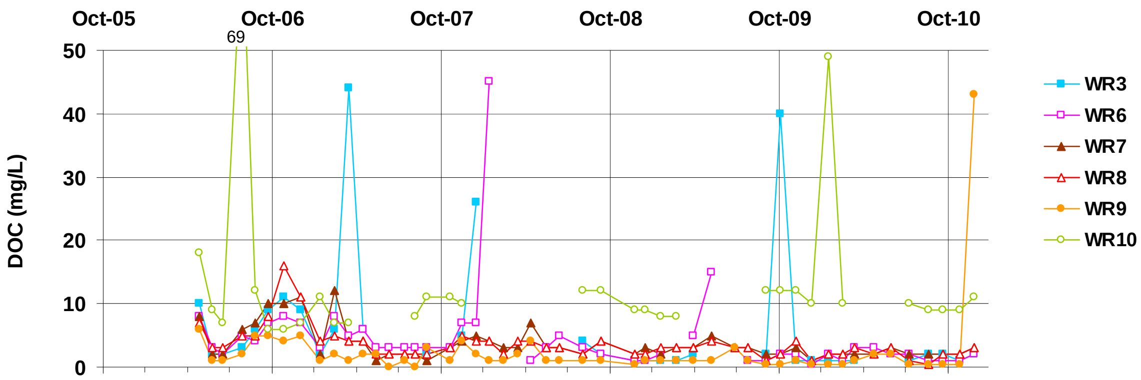


Figure 21: Mean ± standard deviation of dissolved organic carbon at the WTWs (in mg/L).

Table 9: Summary statistics for dissolved organic carbon (in mg/L).

Dissolved Organic Carbon (DOC), (mg/L)															
	Upper Transect						Lower Transect								
	WR3	**WR6**	**WR7**	**WR8**	**WR9**	**WR10**	**WR16**	**WR15**	**WR14**	**WR13**	**WR12**	**WR11**	**UT**	**LT**	**All**
Median	2.0	3.0	3.0	3.0	1.0	10.0	2.0	1.0	1.0	1.0	1.0	1.0	3.0	1.0	2.0
Mean	**6.2**	**4.5**	**3.6**	**3.5**	**2.5**	**12.8**	**2.3**	**1.6**	**1.6**	**1.6**	**1.7**	**1.8**	**5.0**	**1.8**	**3.3**
Stdev	10.3	6.7	2.6	2.6	6.0	12.6	1.6	1.2	1.4	1.7	1.2	1.5	7.7	1.5	5.6
CV	167	150	72	73	245	98	69	76	88	106	74	83	155	83	171
Min	1.0	0.5	1.0	0.5	0.0	6.0	1.0	1.0	0.5	0.0	0.5	0.5	0.0	0.0	0.0
Max	44.0	45.0	12.0	16.0	43.0	69.0	7.0	6.0	6.0	9.0	6.0	7.0	69.0	9.0	69.0
Range	43.0	44.5	11.0	15.5	43.0	63.0	6.0	5.0	5.5	9.0	5.5	6.5	69.0	9.0	69.0
n	34	46	50	50	50	32	50	50	50	50	50	50	262	300	562



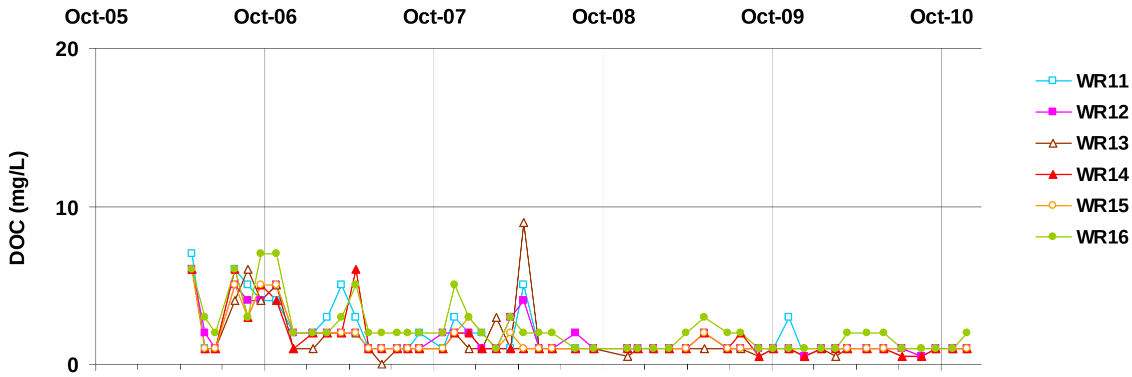


Figure 22: Dissolved organic carbon time series for the WTWs (in mg/L). Note the difference in vertical scale of charts.

The overall mean DOC concentration of all 562 groundwater samples analysed between May 2006 and December 2010 was 3.3 mg/L, with a standard deviation of 5.6 mg/L. This high variation is also reflected in the overall median being only 2.0 mg/L. Note that DOC concentrations were substantially lower than DIC concentrations; the overall mean by 60% and the overall median by 41% (see Table 8).

The mean DOC concentration of the Upper Transect samples was nearly three times as high (5.0 mg/L) than the mean DOC concentration of the Lower Transect samples (1.8 mg/L). The higher Upper Transect mean is partly due to a number of very high concentration peaks observed at WR3, WR6, WR9 and WR10. Disregarding all concentration peaks > 15 mg/L, the mean DOC concentration still remains more than twice as high at the Upper Transect (3.8 mg/L) as compared to the Lower Transect (1.8 mg/L).

With 12.8 mg/L, well WR10 (located at the NE end of the Upper Transect) had by far the highest mean DOC concentration of all wells. While two DOC concentration peaks (69 and 49 mg/L) contribute to this high mean, it is largely due to DOC concentrations at this well generally fluctuating around the 10 mg/L level (Fig. 22).

3.2 Multilevel wells (MLWs)

3.2.1 Vertical groundwater redox-gradient (exemplified by WR20)

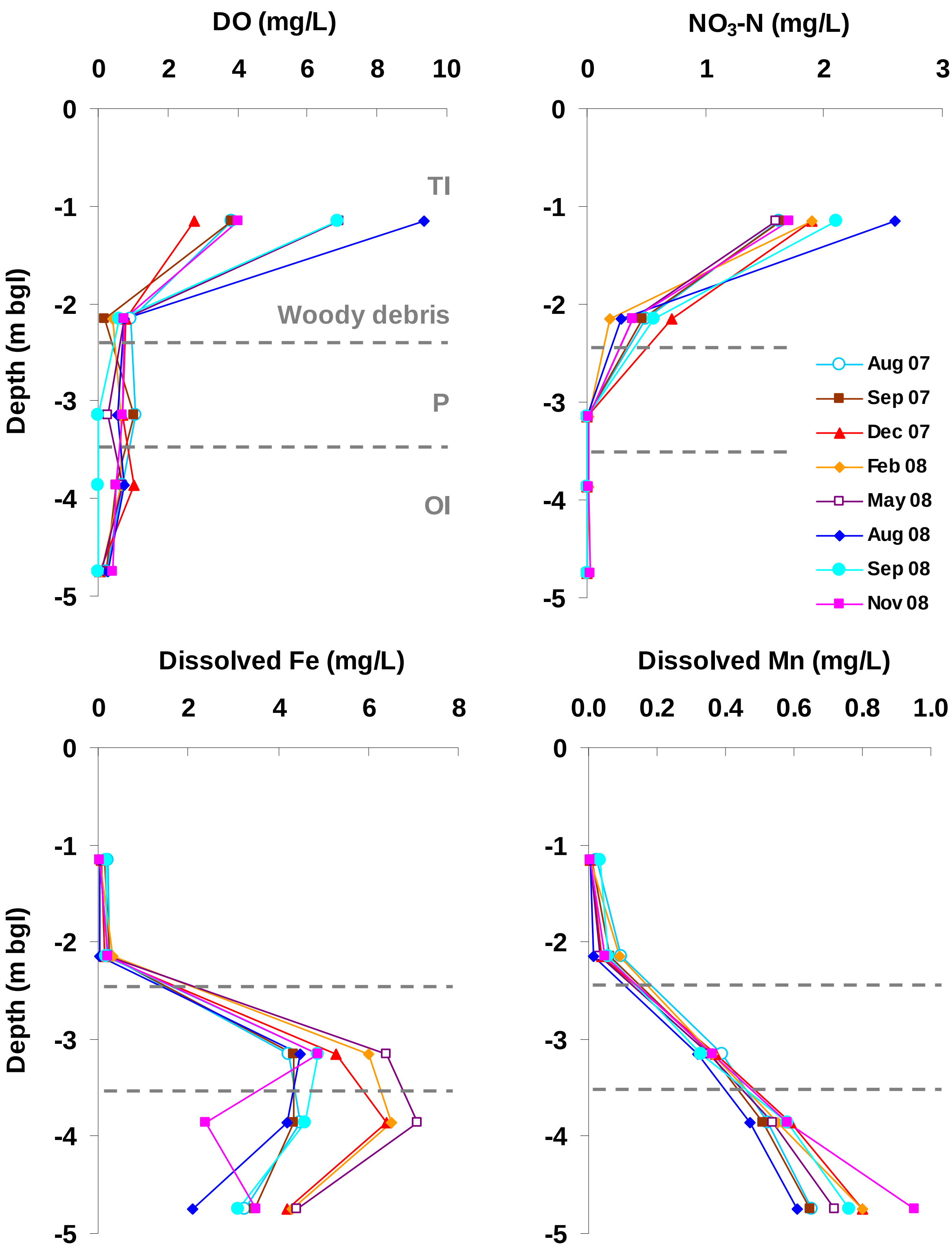


Figure 23: Depth profiles of dissolved oxygen (DO), nitrate nitrogen (NO_3-N), dissolved iron (Diss. Fe), and dissolved manganese (Diss. Mn) at MLW WR20.

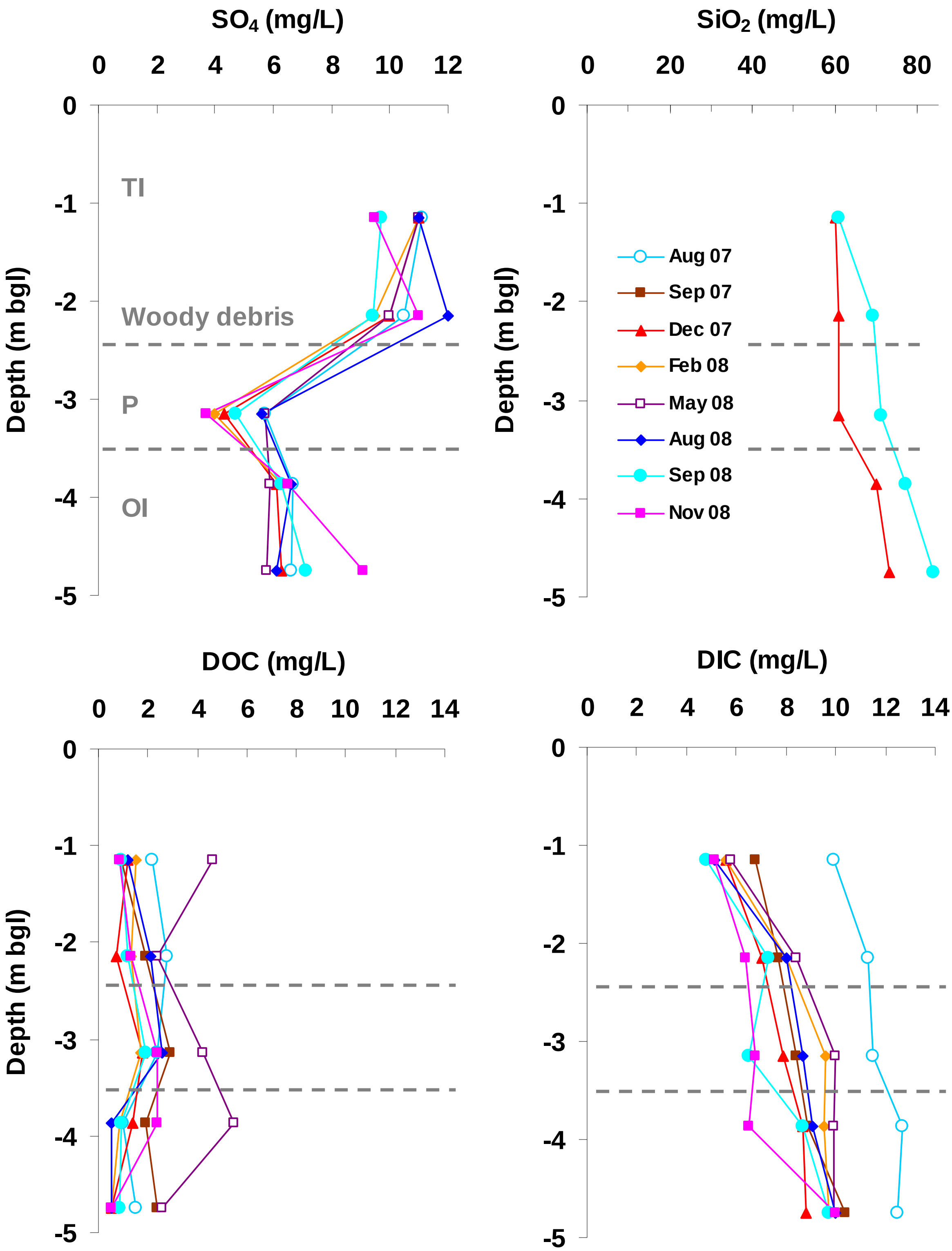


Figure 24: Depth profiles of sulphate (SO_4), silica (SiO_2), dissolved organic carbon (DOC), and dissolved inorganic carbon (DIC) at MLW WR20.

The suite of analysed redox sensitive parameters allows deducing which of the redox reactions and corresponding electron donors (O_2, NO_3^-, Mn^{4+}, Fe^{3+}, SO_4^{2-}, CH_4) listed in Box 1, Section 2.3.2, are likely to be the dominant ones in the groundwater sampled in a particular well. Given that thermodynamic equilibrium does not normally exist in natural systems, it is possible that some of the reactions occur concurrently. Evaluating the depth profiles from MLW WR20, the following conclusions regarding the vertical groundwater redox-gradient at that location can be drawn:

The dissolved oxygen profiles in Fig. 23 demonstrate that the oxidation status of water close to the top of the saturated zone (WR20-1) varied over time, albeit DO levels never dropped below 2.0 mg/L. In agreement with published literature (see Korom, 1992), an empirical relationship established at the Waihora well field between DO and NO_3-N concentrations suggests that 2.0 mg/L DO is a threshold below which conditions become conducive to denitrification (see Fig. 25). Accordingly, NO_3-N was detected in the groundwater at this depth and dissolved iron and dissolved manganese were absent. The sulphate concentration (Fig. 24) was in the range typical for oxidised groundwater from the Waihora well field. All these data indicate that aerobic decomposition of organic matter with oxygen as the terminal electron acceptor is the key microbial redox process at shallow saturated depth in the Taupo Ignimbrite material at WR20 (see Eq. 1 in Box 1, Section 2.3.2).

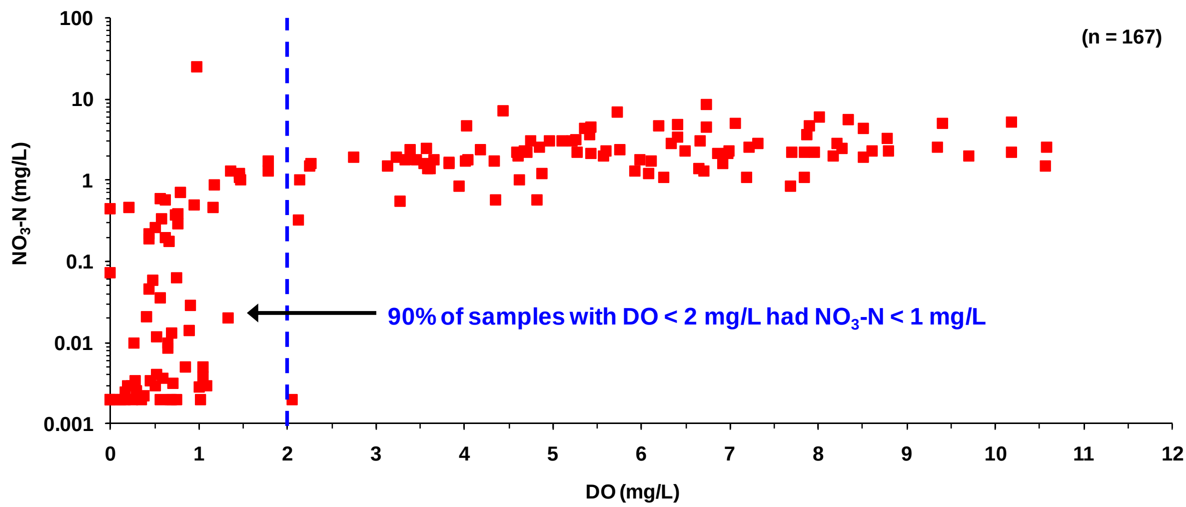


Figure 25: Relationship between NO_3-N and DO in MLW groundwater samples from the Waihora well field (n = 167).

Dissolved oxygen was essentially absent at the base of Taupo Ignimbrite sampled at WR20-2 (Fig. 23), indicating that aerobic decomposition had ceased to be a viable option for microbial energy gain at this depth. Nitrate persisted at levels below 1 mg/L, but was never completely absent (Fig. 23). Dissolved manganese occurred at marginally elevated concentrations, but dissolved iron was not elevated. Sulphate concentrations were also similar to those measured in the shallower groundwater sampled at WR20-1. These results suggest that nitrate is the terminal electron acceptor in groundwater sampled at the base of the Taupo Ignimbrite strata at WR20-2; in other words, heterotrophic denitrification is the process most likely responsible for the substantially diminished nitrate concentration of this 'reduced' groundwater (see Eq. 2 in Box 1, Section 2.3.2).

Groundwater in the Palaeosol, as monitored at WR20-3, was highly electro-chemically reduced. In addition to dissolved oxygen, nitrate was also absent at this depth. This suggests that after aerobic decomposition, heterotrophic denitrification had also ceased to be a viable process for microbial energy generation. Concentrations of dissolved organic carbon tended to be slightly higher compared to the groundwater sampled in Taupo Ignimbrite above and Oruanui Ignimbrite below (Fig. 24), indicating that the relict soil organic matter in the Palaeosol releases some dissolved organic carbon. Dissolved iron and dissolved manganese levels were significantly elevated and sulphate concentrations were lower than in overlying groundwater. These data suggest that manganese reduction, ferric iron reduction, and sulphate reduction had all affected the groundwater sampled at this depth, with sulphate presumably being the main terminal electron acceptor (see Eqs. 3 - 5 in Box 1).

The combination of redox-indicators provided a somewhat ambiguous signal at greater depths (i.e. within the Oruanui Ignimbrite), which complicates identification of the terminal electron acceptor. Somewhat higher sulphate concentrations than observed in the Palaeosol suggest redox conditions in the Oruanui Ignimbrite may be less reductive than within the Palaeosol. However, concentrations of dissolved manganese continued to increase in the two Oruanui Ignimbrite sampling depths (WR20-4, WR20-5) and dissolved iron concentrations at WR20-4 remained similar to their Palaeosol level (WR20-3) before dropping back (WR20-5). Notwithstanding some ambiguity, groundwater in Oruanui Ignimbrite appears sufficiently reductive to reduce any nitrate that might enter the system.

The silica profiles available for two sampling dates (Fig. 24) indicate that the occurrence of reduced groundwater at shallow depths cannot be explained by the gradual development of reduced conditions with increasing groundwater age (as observed in some deep aquifers). While there is evidently a strong redox-gradient from the top of the saturated Taupo Ignimbrite (WR20-1) to its base (WR20-2) and into the Palaeosol (WR20-3), silica data suggest that the groundwater age throughout that depth range is relatively stable. A stronger groundwater age gradient appears to exist between the Palaeosol (WR20-3) and the top of the underlying Oruanui Ignimbrite (WR20-4) and further into the Oruanui Ignimbrite stratum (WR20-5).

Dissolved organic carbon (DOC) recharging from the soil zone is one of the potential carbon sources enabling heterotrophic microbial activity in the saturated zone. Mean DOC concentrations in the WR20 profile did, however, not show a clear tendency of decreasing concentrations with increasing depth (Fig. 24). The mean DOC concentration varied only little between the wells, with 1.7 mg/L at both Taupo Ignimbrite wells, 2.5 mg/L in the Palaeosol well, 1.8 mg/L in the upper Oruanui Ignimbrite well, and 1.2 mg/L in the deeper Oruanui Ignimbrite well. While the relict soil organic matter of the Palaeosol is presumably the reason for the slightly elevated DOC concentrations in the groundwater sampled at this depth (WR20-3), no such effect was associated with the woody debris present at the base of the Taupo Ignimbrite (WR20-2).

Although the mean concentration of dissolved organic carbon did not show a consistent decrease with increasing depth, the mean concentration of dissolved inorganic carbon (DIC) increased steadily with depth. This increase reflects the generation of DIC (mainly HCO_3^-) by each of the redox processes listed in Box 1. The overall increase was 4.0 mg/L DIC, from 6.1 mg/L in the groundwater from the upper Taupo Ignimbrite stratum to 10.1 mg/L in the deeper Oruanui Ignimbrite stratum. The strongest increase occurred within the Taupo Ignimbrite stratum, corresponding with the strongest decrease in dissolved oxygen and nitrate (Fig. 23).

The vertical water chemistry profiles plot for WR20 in Figs. 23 and 24 highlight the advantage of using a MLW set-up with short well screens for monitoring the subsurface compared to a conventional WTW set-up with a single, long screen, for which any vertical stratification would go undetected.

Based on data from six MLWs located within the Upper and Lower Transects (Fig. 3), we therefore investigate in the next section whether redox-gradients as observed at WR20 also occur there.

3.2.2 Data from MLWs located in the Upper and Lower Transects

As for the **Upper Transect**, Figure 26 demonstrates that the uppermost groundwater at MLW WR22 (next to WR3) can seasonally be well-oxidised and nitrate-bearing, while deeper groundwater was consistently oxygen and nitrate depleted. As at WR20, the upper well is screened in the Taupo Ignimbrite stratum near the top of the saturated zone and the deeper well near the TI base, where woody debris is present.

The data from the three wells at MLW WR21 (next to WR9) show temporal variation in oxygen profiles, but dissolved oxygen concentrations remained above 2 mg/L at most sampling dates even in the Oruanui Ignimbrite material at depth (Fig. 26). The groundwater level resided at this location predominantly below the Taupo Ignimbrite layer, which presumably explains why no woody debris was present (see Fig. 4).

Data from WR27 (between WR7 and WR8) are not presented in a figure, as the single well screened in the Oruanui Ignimbrite stratum was only sampled three times. The groundwater sampled there was consistently oxygen and nitrate depleted.

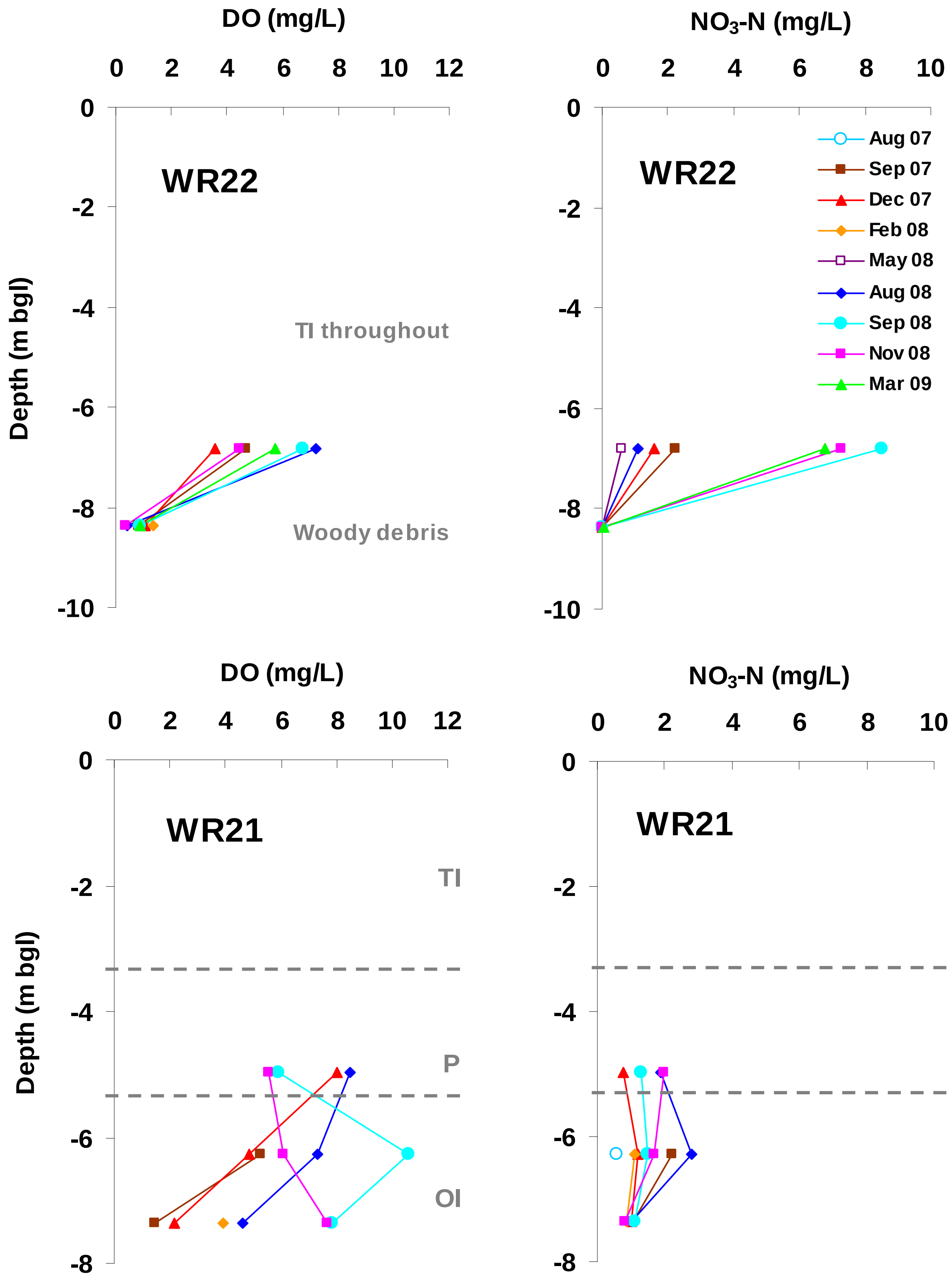


Figure 26: Depth profiles of dissolved oxygen (DO) and nitrate nitrogen (NO_3-N), at MLWs WR22 and WR21.

At the **Lower Transect**, consistently oxidised conditions and only a very weak redox-gradient were observed at MLW WR18 (Fig. 27), which is located in the centre of the Lower Transect between

WTWs WR14 and WR13 at a location where no Palaeosol or woody debris was detected when coring. Both WR18 well screens draw groundwater from Oruanui Ignimbrite material.

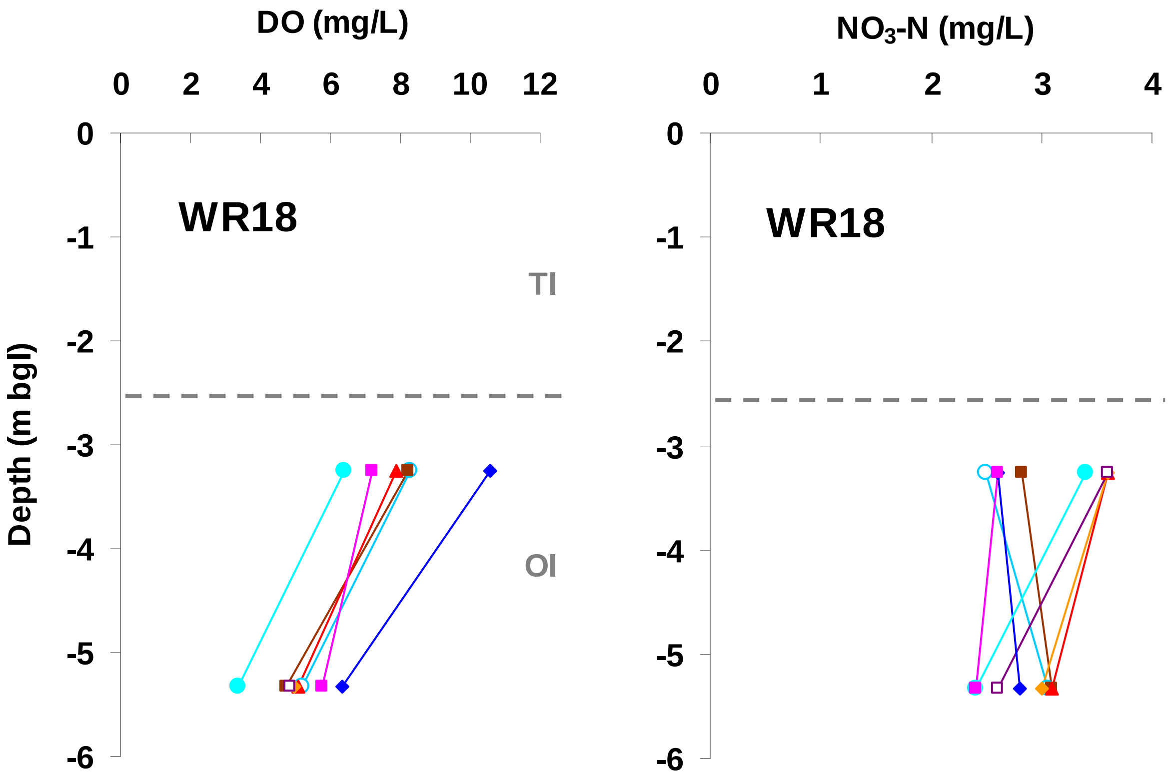


Figure 27: Depth profiles of dissolved oxygen (DO) and nitrate nitrogen (NO_3-N), at MLW WR18.

Consistently reduced conditions were observed in the deeper groundwater sampled at MLWs WR25 (near WTWs WR12 and WR11) and WR26 (next to WTW WR15). In contrast to WR20 and WR22, these wells are not screened at the very base of the Taupo Ignimbrite material, but woody debris was already present at the screened depth range (see Fig. 3). The shallower well screens at WR25 and WR26 are both located in Taupo Ignimbrite material and in similar distance to the woody debris below and the top of the saturated zone above (Fig. 3). However, groundwater in the shallow depth of WR26 was consistently more oxidised than the shallowest groundwater sampled at WR25 (Fig. 28). Correspondingly, nitrate levels at WR26 were always higher than at WR25, where nitrate concentrations near the detection limit occurred.

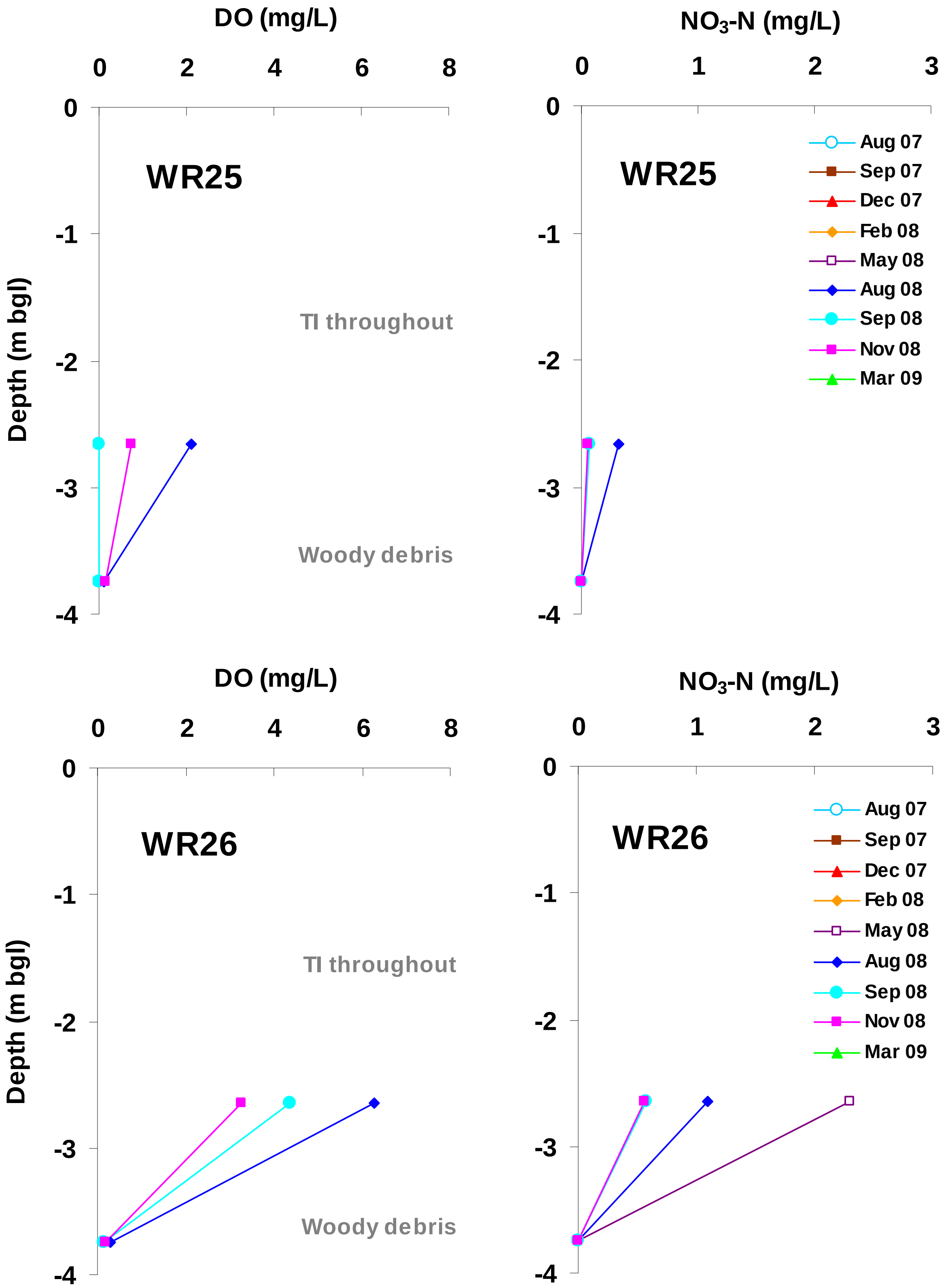


Figure 28: Depth profiles of dissolved oxygen (DO) and nitrate nitrogen (NO_3-N), at MLWs WR25 and WR26.

From the data presented here, and additionally including results from four MLWs (WR23, WR17, WR19, WR24) that are like WR20 located along the Downslope Transect (see Figs. 2 and 29), the following conclusions regarding the relationship between groundwater redox status, carbon source and lithological stratigraphy can be drawn:

Reduced groundwater, devoid of nitrate, occurred consistently at the **base of the Taupo Ignimbrite** stratum at those locations where woody debris was present (WR20-2, WR22-2, WR26-2, WR25-2). This observation strongly suggests that the woody debris represents a carbon source that encourages microbial activity at this depth to such a degree that at first dissolved oxygen becomes depleted through aerobic decomposition and subsequently nitrate gets reduced through heterotrophic denitrification. However, even in the shallowest sampled groundwater, DO concentrations were in most instances already below their equilibrium level with the atmosphere (approx. 11 mg/L at 11°C). This indicates that oxygen consumption must have been greater than replenishment from the atmosphere even above the depth where the woody debris was present. Given that the Taupo Ignimbrite stratum contains hardly any resident organic carbon, apart from the woody debris at its base, organic carbon leached down from the soil zone is the most likely carbon source for microbial respiration in the shallowest groundwater.

At two locations along the Lower Transect, reduced groundwater occurred already at **shallower depth in the Taupo Ignimbrite** stratum (at WR26-1, and particularly at WR25-1), at least 0.5 m above the depth where woody debris was found. At one other location, groundwater at the base of the TI stratum was seasonally reduced, in spite of woody debris being absent there (WR19-1). These observations could potentially be explained by reduction having occurred in the presence of woody debris at a location along the groundwater flow path upslope of these wells. However, based on the available knowledge about the spatial distribution of woody debris combined with the modelling of the groundwater flow, this possibility seems unlikely (Stenger et al., 2010). It would thus appear that organic carbon leached from the soil zone may be responsible on its own for the occurrence of reduced groundwater at these locations.

The groundwater sampled from the **Palaeosol** stratum at wells WR21-1 and WR24-1 (see Fig. 29) was consistently oxidised and nitrate-bearing. This suggests that the soil organic matter content of this stratum alone does not provide enough carbon to induce sufficiently reduced conditions for denitrification to occur. Groundwater sampled from the P stratum at WR20-3 was strongly reduced, but most of the nitrate reduction and virtually all oxygen consumption had already occurred at the base of the overlying Taupo Ignimbrite stratum (Fig. 23). In contrast to WR21 and WR24, woody debris was present at the base of the TI stratum at WR20.

The redox status of groundwater sampled from the **Oruanui Ignimbrite** stratum ranged from well oxidised to strongly reduced. While DO concentrations generally decreased with increasing depth within the OI stratum, oxidised conditions even in the deepest well prevailed at WR21, WR23, WR18 and WR17 (see Fig. 31). These four well locations have in common that no woody debris was present in their Taupo Ignimbrite stratum.

Five wells screened in the OI stratum drew reduced groundwater; predominantly at WR19-2 and consistently at WR20-4, WR20-5, WR24-2, and WR27. The depth profiles from WR20 (Fig. 23) demonstrate that the reduced groundwater sampled at WR20-4 and WR20-5 was overlain by approx. 2 m of already reduced groundwater residing in the TI and P strata. However, the somewhat higher sulphate concentrations in the OI stratum as compared to the P stratum and the decreasing concentration of dissolved iron within the OI stratum suggest that the groundwater in the OI does not exclusively arrive there by vertical flow. Lateral flow of somewhat less reduced water from upslope locations appears to occur. The somewhat steeper increase in silica concentrations below the P stratum supports this notion (Fig. 24).

Woody debris at the base of the TI stratum is presumably the carbon source responsible for the consistently reduced groundwater sampled from the OI stratum at well WR27 (see Fig. 3).

Reduced groundwater in the OI stratum was found underlying oxidised shallower groundwater temporarily at WR19 and consistently WR24 (see Fig. 29). As there is no identifiable carbon source in these profiles that could explain the strong vertical redox-gradients observed at these locations, the deeper groundwater is assumed to have been reduced along its flow path somewhere upslope of the sampling location. This assumption is backed by relatively steep silica concentration gradients between the shallower and deeper wells at these two locations (data not shown).

The relationship between the groundwater redox status and the hydraulic properties of the material surrounding the well screen forms part of Lincoln Ventures' ongoing research. The limited data available to date shows that the saturated hydraulic conductivity can vary by two orders of magnitude within the same stratum (approx. 0.1 to 10 m/day). Reduced groundwater occurred more commonly where the saturated hydraulic conductivity was low (data not shown). However, oxidised groundwater can also occur under such conditions (e.g. at WR26-1, WR19-2) and vastly different redox conditions have been observed between locations with identical hydraulic conductivity (e.g. WR20-1 vs. WR20-2).

<u>In summary, these data suggest that:</u>

- Woody debris residing at the base of the TI stratum is an important, but not the only carbon source inducing reduced conditions. Carbon residing in the Palaeosol appears to be of lesser importance for the groundwater system's assimilative capacity for nitrate than carbon derived from the topsoil.
- Sampling reduced groundwater at a particular well location from a particular stratum does not necessarily mean that reductive processes are active at that well location or in that stratum. Wherever groundwater flow is not entirely vertical, the reductive processes can have occurred somewhere along the groundwater flow path upslope of the sampling location.
- While reduced groundwater was more commonly found at locations with low saturated hydraulic conductivity, the high degree of variation in the limited data available to date necessitates further investigations into the relationship between groundwater redox status and hydraulic properties of the strata.

4 DISCUSSION

4.1 Groundwater levels

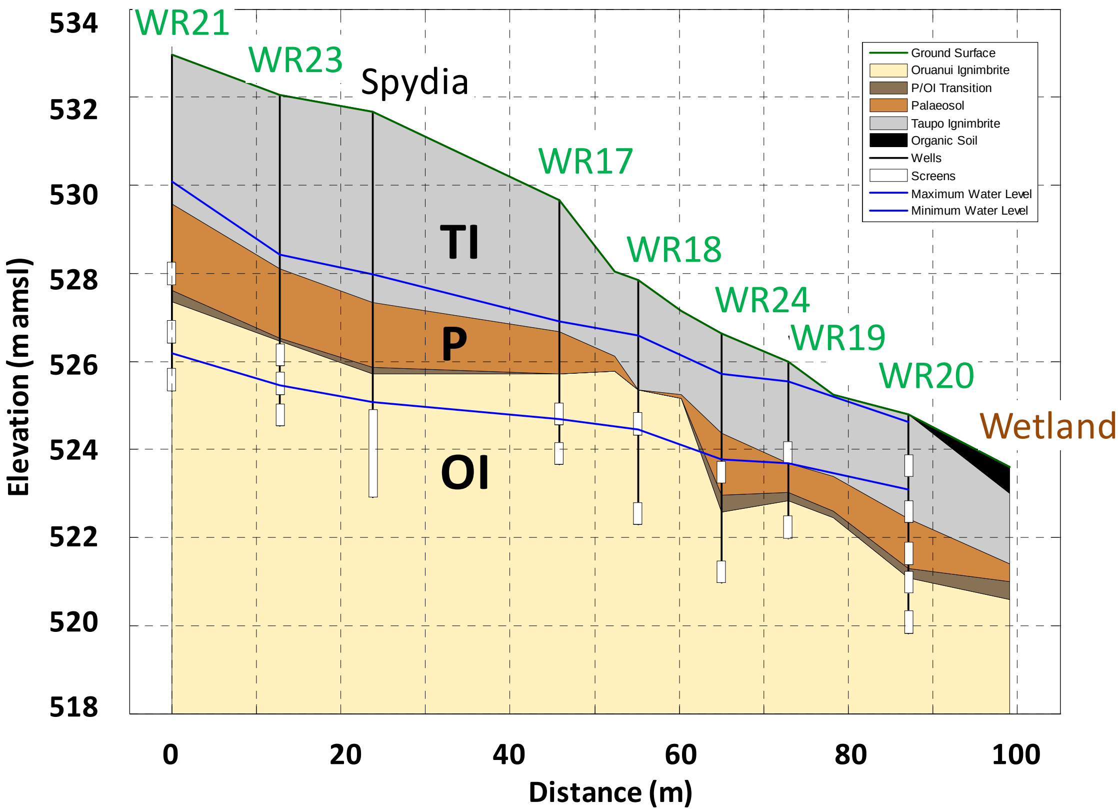


Figure 29: Vertical cross-section of the Downhill MLW transect, showing lithology and maximum and minimum water levels.

For two reasons, groundwater levels fluctuated less at the Lower Transect (1.5 – 1.8 m) than at the Upper Transect (> 2.2m; Tab. 2). Firstly, the Lower Transect is located closer to the wetland, which acts as a local constant head boundary about which the water table effectively hinges (Fig. 29). Note that the Upper Transect intersects the Downhill Transect on the upper slope at WR21, while the Lower Transect intersects at WR18 on the lower slope. Secondly, different hydraulic properties, resulting from different lithological strata in the screen range, additionally contribute to the greater amplitude observed at wells WR9 and WR10 in the Upper Transect (Fig. 6).

To allow for a direct comparison, representative groundwater level time series (recorded at 15 min resolution) are presented in Figure 30. The difference in water level amplitude between WR13 at the Lower Transect (1.7 m) and WR7 at the Upper Transect (2.2 m) is largely due to their different distance to the wetland, as both wells are at least predominantly screened in the Taupo Ignimbrite stratum. In contrast, the difference in amplitude between WR7 (2.2 m) and WR9 (4.2 m) at the Upper Transect reflects the effect of different strata. WR7 mostly screens the Taupo Ignimbrite stratum, whereas the groundwater level fluctuations at WR9 reflect the integrated hydraulic characteristics of Taupo Ignimbrite, Palaeosol and Oruanui Ignimbrite materials. Palaeosol and Oruanui Ignimbrite materials both have lower effective storage characteristics than Taupo Ignimbrite; Palaeosols due to their finer texture and Oruanui Ignimbrites due to their lower total porosity. This lower effective storage presumably explains the greater groundwater level amplitude observed at WR9 as compared to the four wells at the Upper Transect that are entirely or at least predominantly screened in the Taupo Ignimbrite stratum. While no lithology information is available for well WR10, the water level fluctuations observed in this well would suggest that the screen reaches into the Palaeosol stratum (Fig. 6).

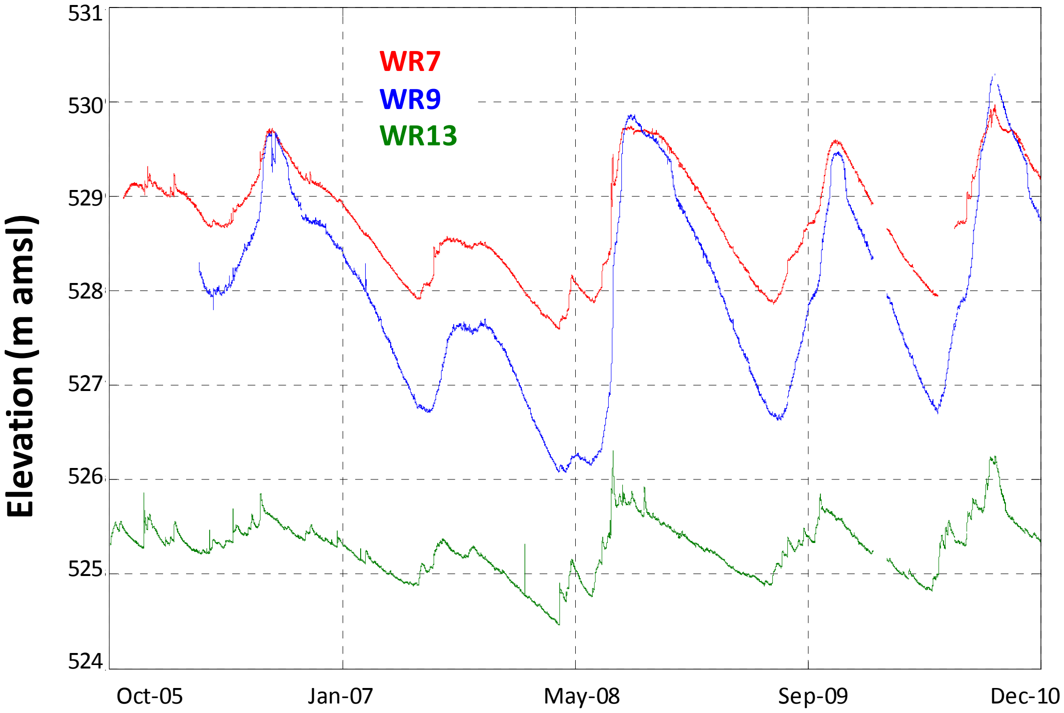


Figure 30: Water level dynamics automatically recorded with pressure sensors at WR7 and WR9 in the Upper Transect and WR13 in the Lower Transect.

The spikiness of the WR13 groundwater level data (compared to the smoother wave forms of WR7 and WR9 data) is due to the difference in the vadose zone thickness between the Upper and Lower Transects. The water level at WR13 is typically just 2.5 m below the ground surface (Tab. 2), and from Figure 30 it can be inferred that groundwater levels respond very rapidly to rain. In contrast, the attenuated peaks in the data of WR7 and WR9 reflect the smoothing effect of greater water storage potential in a deeper vadose zone.

4.2 Groundwater chemistry

The spatio-temporal variation of some groundwater chemistry parameters (excluding nitrate) is briefly discussed in Section 4.2.1, focusing on those well locations and parameters that showed a high degree of variability. The subsequent Section 4.2.2 focuses in greater detail on the interpretation of the measured nitrate concentrations, and particularly on the effect of denitrification on some of the time series. In Section 4.2.3, we summarise the current state of our understanding regarding the redox stratification of shallow groundwater at the Upper and Lower Transects. Finally, in Section 4.2.3, a comparison is provided between the nitrate concentrations measured in shallow groundwater and root zone losses estimated using the OVERSEER nutrient balancing model.

4.2.1 Spatio-temporal variation of selected parameters

Variation within time series of individual wells

The groundwater chemistry time series of individual wells showed in most instances relatively moderate temporal variation, with the majority of observations lying within reasonably narrow ranges. However, a small number of distinct peaks that were often caused by one single sampling date occurred at some locations. They were particularly prominent at WR3, WR6 and WR10 in the Upper Transect and occurred most frequently for DOC (and therefore also DTC) and for NH_4-N. Due to the low absolute concentrations of NH_4-N relative to NO_3-N, most NH_4-N peaks are of no concern from a nitrogen mass point of view. However, sometimes they can help to interpret DOC and NO_3-N peaks.

The three extremely high dissolved organic carbon peaks observed at WR3 (Mar 07, Dec 07, and Oct 09) all coincided with small ammonia nitrogen peaks and with water columns in the well being smaller than 0.5 m at the time of sampling. Such low water levels mean that any occurring localised plume strongly affects the sample as less mixing of groundwater occurs than under high water level conditions. Particularly the DOC and NH_4-N peak in October 2009 might be related to the effect of a urine patch reaching the saturated zone, as NO_3-N steadily increased over the following months to reach a peak in February 2010. This could be due to gradual nitrification of urine-derived ammonia nitrogen (Fig. 38). The two NH_4-N peaks observed at WR6 (Jun 08, May 09) also occurred at low water levels and coincided with the two lowest NO_3-N concentrations measured at that location. This could be explained by mineralisation of organic nitrogen being halted at the nitrification stage due to oxygen depleted conditions. However, DOC only showed a corresponding peak in May 2009. The highest DOC peak observed at that location occurred in January 2008, just before the well dried up. As any artefact that possibly could be caused by material accumulating in the bottom of the well should have been minimised by well purging, it would appear that the high concentration reflected real conditions occurring at the top of the saturated zone at that date. The two DOC peaks recorded at WR10 (Aug 06, Jan 10) do not coincide with minima or maxima of any other measured parameter.

Variation within transects

In some instances, differences between wells were largely due to differences in their 'base level' rather than to differences in concentration peaks. Over extended periods enhanced electrical conductivity values were observed at well WR3 and to a lesser degree at WR6 and WR10 (Fig. 16). However, while there was a reasonably strong correlation between EC and NO_3-N at WR3 (ignoring one outlier), no strong correlations with any of the measured parameters were found for WR6 and WR10. This implies that ions other than the measured ones were responsible for these temporarily enhanced values.

The existence of woody debris, which was noted during well installation at WR7, WR8, and WR15, was not reflected in the dissolved organic carbon concentrations measured at these locations (Fig. 21). Equally, the Palaeosol occurring at WR9 did not have any discernible effect on the DOC concentrations in this well, which were actually the lowest of the Upper Transect. No explanation can be offered for the observation that the neighbouring well WR10 had consistently by far the highest DOC concentrations of all wells (mean 12.8 mg/L).

Variation between transects

It is noteworthy that dissolved organic carbon was generally higher in groundwater at the Upper Transect as compared to the Lower Transect (Fig. 21), even if the few concentration peaks discussed above are ignored (Fig. 22). Assuming that leaching from the soil zone is the main source of DOC at both transects, one might have expected lower concentrations at the Upper Transect, as the deeper vadose zone allows for more mineralisation before the saturated zone is reached. However, this notion only applies to conditions that are dominated by strictly vertical DOC transport. The lower DOC concentrations at the Lower Transect reflect presumably that a high proportion of the groundwater sampled at these wells was recharged further up on the slope and arrived at the well screen on much longer lateral flow paths, allowing for a greater degree of mineralisation.

4.2.2 Effect of groundwater denitrification on nitrate nitrogen concentrations

The overall mean nitrate nitrogen concentration of all 682 groundwater samples analysed during the 6-year period from November 2004 to December 2010 was 2.07 mg/L. While this concentration is low compared to the drinking water standard (10 mg/L), it is of great significance in the Lake Taupo catchment, as it is the goal of Waikato Regional Council's Regional Plan Variation 5 to restrict the total N concentration of the lake water to 0.07 mg/L.

In spite of all groundwater samples originating from a small area of approximately 3300 m^2 within the same paddock, substantial spatial variation is evident in the nitrate nitrogen data. Mean concentrations over the entire 6-year monitoring period ranged from 0.49 mg/L NO_3-N at WR7 to 6.44 mg/L NO_3-N at WR3, which are only 25 m apart (Fig. 34). Spatially and temporally variable losses from the root zone (e.g. urine patches) contribute to the observed variation in measured groundwater concentrations. However, it is also affected by the spatially and temporally varying degree of groundwater denitrification. The degree to which the effect of denitrification is reflected in the monitoring data is influenced by the location of the well screen relative to the groundwater redox-gradient. This aspect will be discussed in detail in Section 4.3.

Denitrification occurring in groundwater

A combination of observations leads us to conclude that the nitrate nitrogen concentrations measured in a few of the water table wells have been affected by denitrification (WR7, WR8, and WR16; possibly also WR15, WR12 and WR11). This denitrification need not have necessarily occurred at the well location; where lateral groundwater flow is significant, it is possible that denitrification occurred somewhere along the groundwater flow path upslope of the well location.

Three strands of information were used to evaluate the likelihood of denitrification having reduced the nitrate concentration of groundwater sampled at a particular WTW location:

1. NO_3-N concentrations measured in groundwater,
2. Knowledge inferred from adjacent MLWs,
3. Dissolved oxygen profiles.

<u>Re. 1</u>: While low nitrate nitrogen concentrations in shallow groundwater can simply reflect low input from the vadose zone, extremely low concentrations (< 0.1 mg/L) are largely restricted to oxygen-depleted groundwater with DO < 1 mg/L and due to denitrification (see Fig. 25).

<u>Re. 2</u>: Nitrate-depleted groundwater was found at all MLWs where woody organic debris from the vegetation destroyed by the 1.8 ka BP Taupo eruption was present. The presence of debris at a WTW location consequently suggested potential for denitrification to occur. In some instances, inferences concerning WTWs could be drawn from groundwater monitoring data from adjacent MLWs.

<u>Re. 3</u>: No dissolved oxygen profiles for the WTWs are available for the 2004 – 2010 monitoring period. However, such profiles were recorded in June 2011 (using a small-diameter optical DO sensor, Fig. 31).

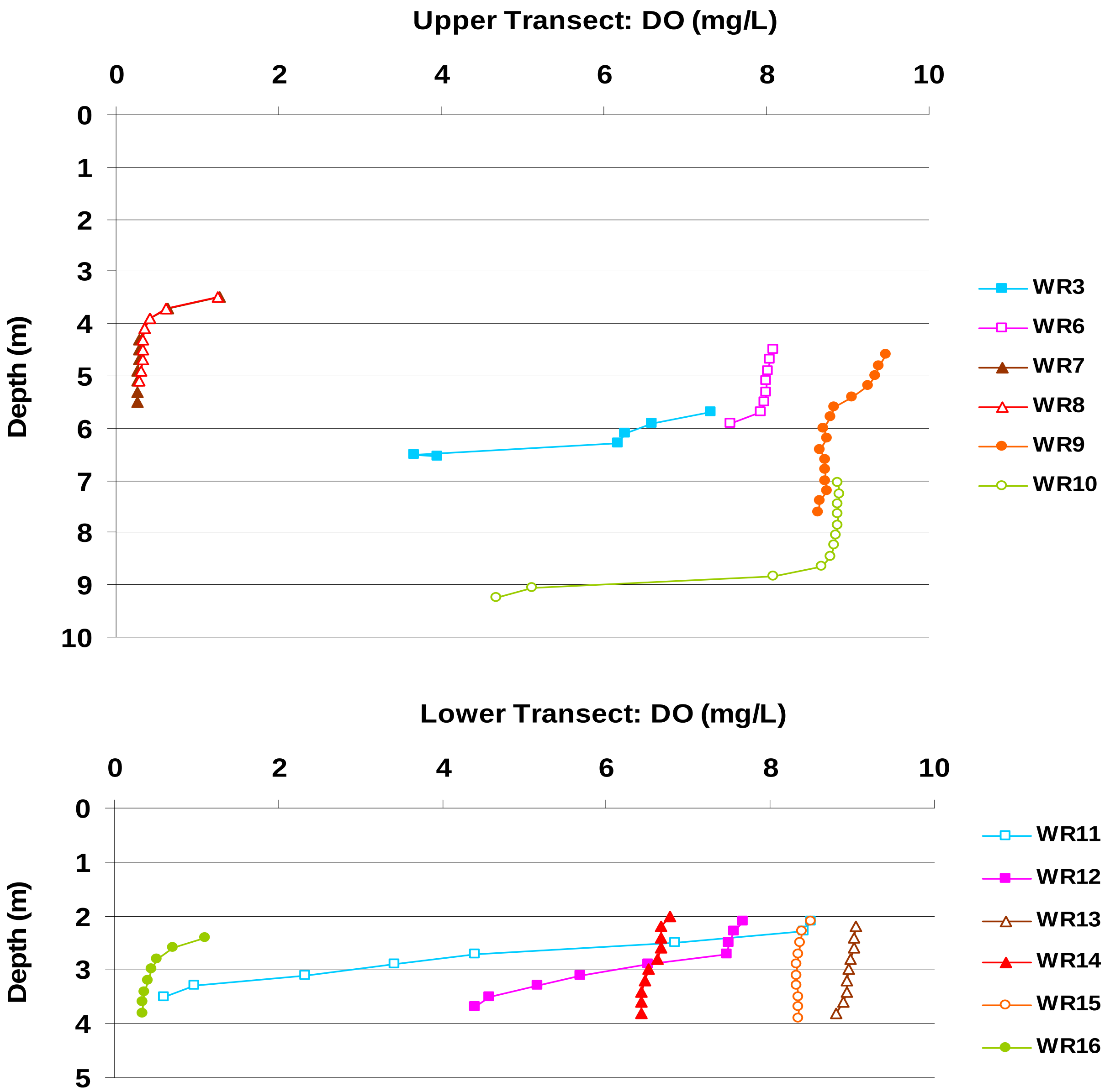


Figure 31: Dissolved oxygen profiles measured in WTWs in June 2011.

Upper Transect

We contend that denitrification is the main reason for the neighbouring wells **WR7 and WR8** having the lowest mean NO_3-N concentrations of all WTWs (Table 3). Particularly in the second half of the monitoring period, the dynamics of nitrate at these locations is characterised by extended periods of extremely low concentrations (< 0.1 mg/L) separated by relatively short-lived concentration peaks Fig. 32). This pattern could be explained by the existence of a usually oxygen and nitrate depleted groundwater system that only gets substantial input of oxidised and nitrate-bearing water from the vadose zone during the main groundwater recharge period. The woody debris that on the Upper Transect had only been documented for these two WTW locations (Fig. 34) is the likely carbon source inducing the reduced conditions.

The water column time series demonstrate that the nitrate peaks at these two wells often occur when the water level starts rising again after its annual minimum. As evident in Fig. 32, annual water level minima are most often observed during June, but depending on the year's weather pattern can also occur as early as April or as late as July. The relatively short-lived nature of the nitrate peaks suggests that the vadose zone at these locations contains nitrate during the initial phases of the recharge period, but gets depleted thereafter. Consistent with the notion of nitrate getting 'flushed out' of the vadose zone at the start of the recharge period, nitrate peaks often occur in August or September and precede water level peaks by 1 - 2 months (Fig. 32).

From the limited amount of MLW data available it cannot be deduced with confidence whether gradually developing denitrification activity already contributes to the decline in nitrate concentrations after the peaks, but it is considered the main reason for the extended period of very low concentrations that follows. While the small diameter of the WTWs did not allow for low-flow sampling to be undertaken during the reporting period, the DO profiles established in June 2011 demonstrated that WR7 and WR8 had DO concentrations below 1.5 mg/L throughout the profile, while no other water table well of the Upper Transect had anywhere concentrations below 3.7 mg/L (Fig. 31).

The observation that extremely low nitrate concentrations (< 0.1 mg/L) were observed at these two sites at times of water level peaks (e.g. Sep 08, Nov 09, Sep 10) suggests that strongly reduced conditions prevailed throughout the whole water column from the top of the saturated zone down to the base of the wells (Fig 32). This notion is in agreement with the DO profile established in June 2011, where DO even in the uppermost saturated zone was already below 2 mg/L (Fig. 31). While the woody debris documented near the base of the wells can explain the existence of reduced groundwater there, it is unlikely to be the carbon source responsible for reduced groundwater present near the top of the saturated zone.

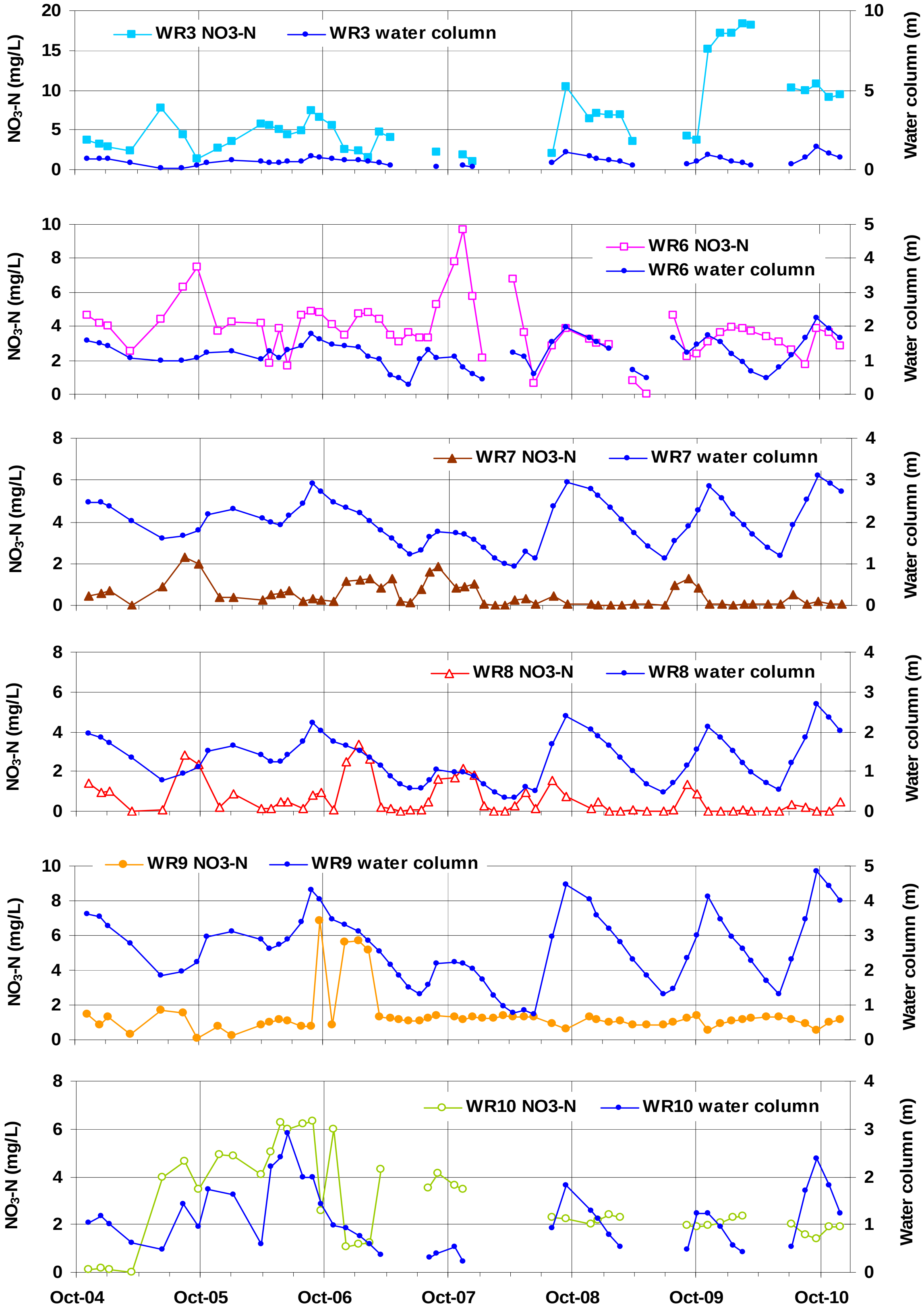


Figure 32: Water column and nitrate nitrogen dynamics at the Upper Transect WTWs. The water column gives the thickness of the groundwater zone that was sampled at each sampling date. Note the variable scale of the NO_3-N axis.

Lower Transect:
While not as pronounced as at WR7 and WR8, nitrate concentrations at **WR16** also appear to have been reduced by denitrification. Particularly low nitrate concentrations were observed from April to June 2007, from November 2007 to March 2008 and from March to June 2010, coinciding with water level minima (Fig. 33). While no woody debris had been noticed during well installation, the DO profile recorded in June 2011 demonstrates that strongly oxygen depleted conditions can occur at this location (Fig. 31). However, the less frequent occurrence of extremely low nitrate concentrations (compared to WR7 and WR8) and data from the neighbouring MLW WR26 suggest that the sampled groundwater was at most sampling dates a mixture of oxidised uppermost and reduced somewhat deeper groundwater (see Section 4.3). Note that apart from three sampling dates with particularly high nitrate peaks, the nitrate concentration and water column graphs shown in Fig. 33 ran nearly parallel to each other, reflecting a positive correlation between nitrate concentration and water level (see figure in Appendix II and discussion in Section 4.3).

Woody debris documented during well installation (see Fig. 35) and the data from the adjacent MLW WR26 (Fig. 28) suggest that denitrification may also occur at **WR15**. However, at least in June 2011 the entire groundwater zone sampled at this well proved to be oxidised (Fig. 31) and no extremely low nitrate nitrogen concentrations were found during the monitoring period (Fig. 33). Both observations could reflect that reduced groundwater may be confined to the base of the well where the debris was found, or may periodically even be absent after significant recharge with oxidised water has occurred (i.e. mainly in winter; Fig. 35).

Data from the nearby MLW WR25 (Fig. 28) and the strong DO gradient observed in June 2011 (Fig. 31) suggest that the deeper part of the **WR11** well screen may draw reduced groundwater. However, nitrate concentrations at WR11 did not show a pattern that would suggest seasonally varying portions of uppermost oxidised and deeper reduced groundwater as previously described for WR16. In contrast to the positive correlation between groundwater level and nitrate concentration at WR16, a weak negative correlation was found at WR11, particularly evident since June 2008 (see Section 4.3).

The largely reduced groundwater found at the nearby MLW WR25 (Fig. 28) suggests that denitrification may have contributed to groundwater sampled at **WR12** having the lowest mean nitrate concentration of all Lower Transect wells (Table 3). However, while the DO profile established in June 2011 indicated a marked decrease in oxygen concentration in the well screen range, DO concentrations still exceeded 4 mg/L at the base of the well. Nitrate concentrations showed little variation at this location (Fig. 33) and consequently were not correlated with the water levels (see Appendix II).

4.2.3 Redox stratification of shallow groundwater

While only circumstantial evidence is available from the water table wells, in Figs. 34 and 35 we summarise in a schematic way the current understanding of the redox conditions in shallow groundwater at the Upper and Lower Transects. As evident from the discussion of individual data sets in the previous section, there are conflicting strands of evidence regarding the redox conditions in some water table wells. It should therefore be noted that the schematics represent our incomplete understanding at the present time. To overcome the existing knowledge gaps, ongoing research focuses on the temporal and spatial variation of DO concentrations in shallow groundwater and on getting a better understanding of the groundwater flow paths at the Waihora well field.

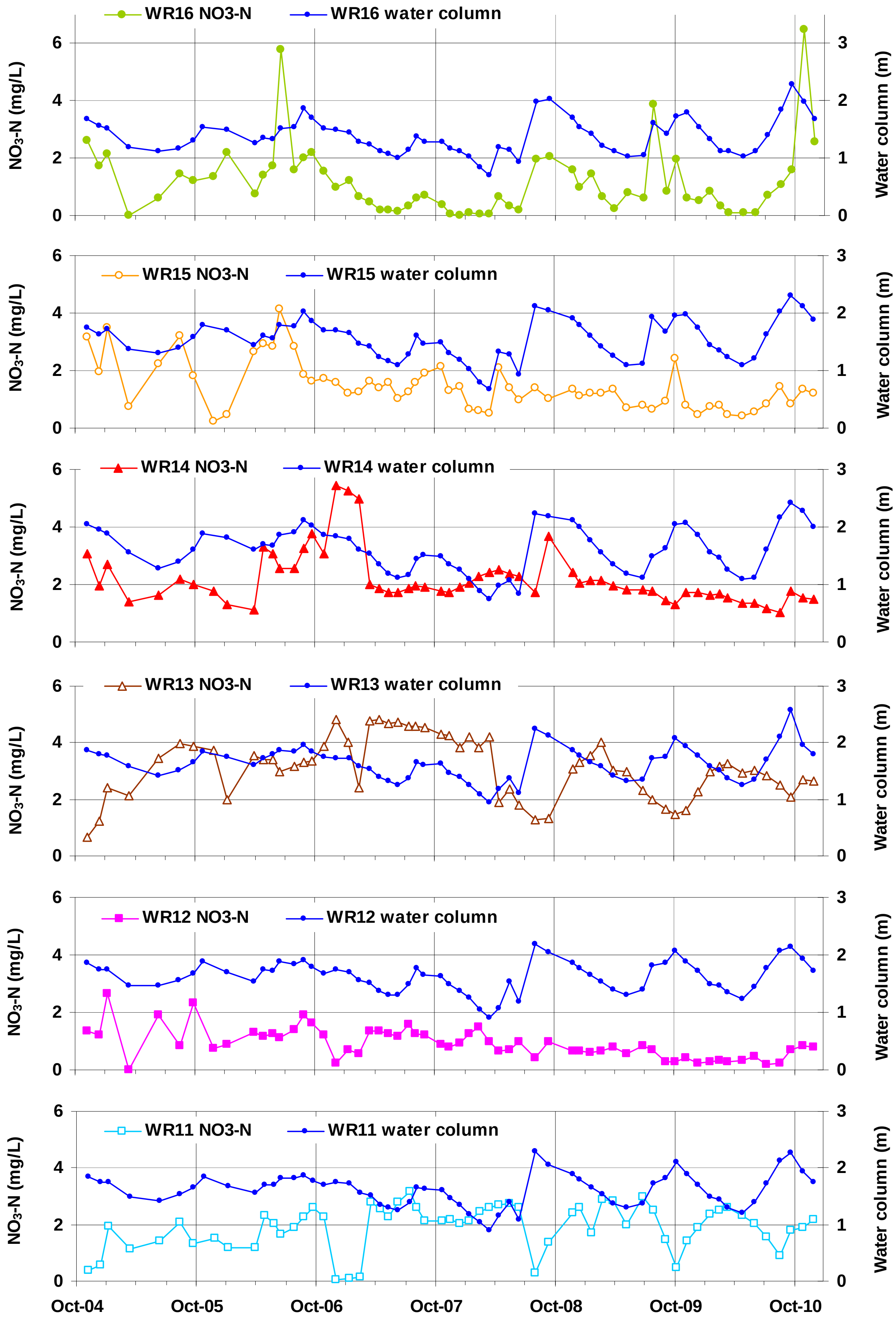


Figure 33: Water column and nitrate nitrogen dynamics at the Lower Transect WTWs.

Redox stratification at the Upper Transect

Near the top of the saturated zone, oxidised groundwater appears to prevail throughout the year at all wells apart from WR7 and WR8 in the centre of the transect (Fig. 34). At the latter two wells, oxidised groundwater seems to be restricted to brief periods at the start of the main groundwater recharge period. The woody debris documented at all four wells where reduced groundwater occurred is presumably the main electron donor for microbial activity. However, it is unlikely to be the sole electron donor, as reduced groundwater at WR7 and WR8 apparently existed up to 2 m above the depth where woody debris resides. It is currently unknown whether reduced groundwater also occurs at greater depth at those well locations where only oxidised groundwater was found within the monitored depth range. Two observations indicate that reduced groundwater may also occur at greater depth at locations without woody debris. Firstly, the dissolved oxygen data from WR21 show that strong oxygen gradients with minima near 2 mg/L existed at some dates (Fig. 26). Secondly, ferrous iron consistently occurred from approx. 6.5 to 30 m below ground level at a borehole located downslope of WR7 (see Box 1, Section 2.3.2).

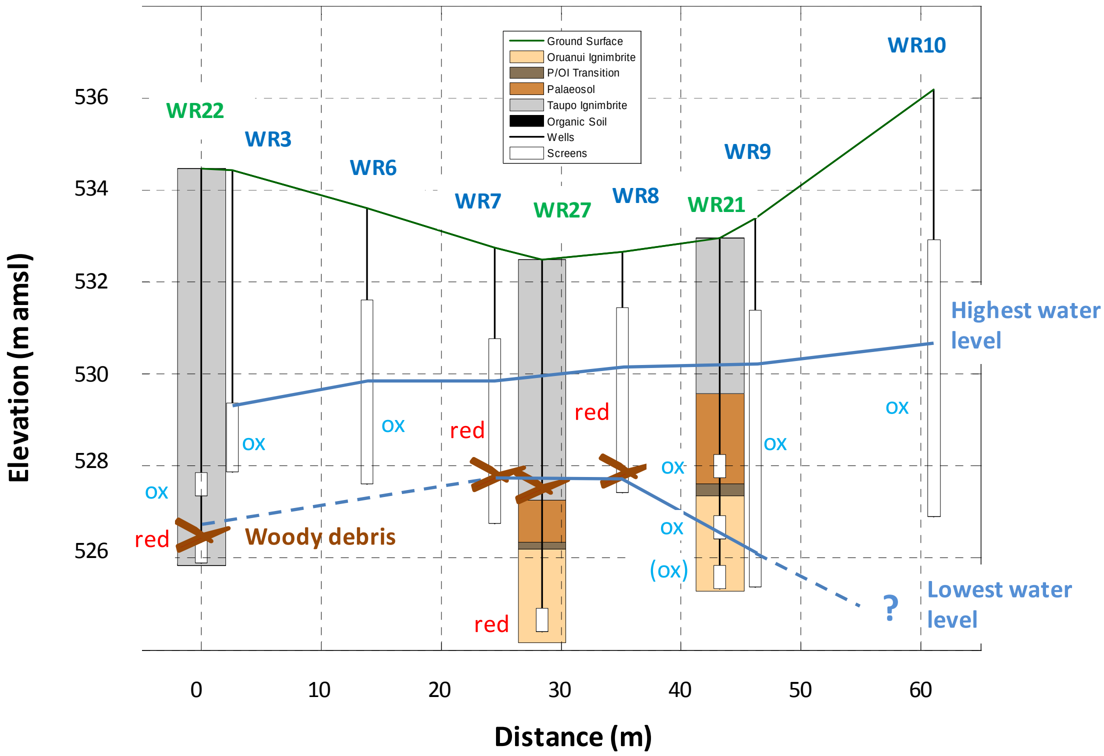
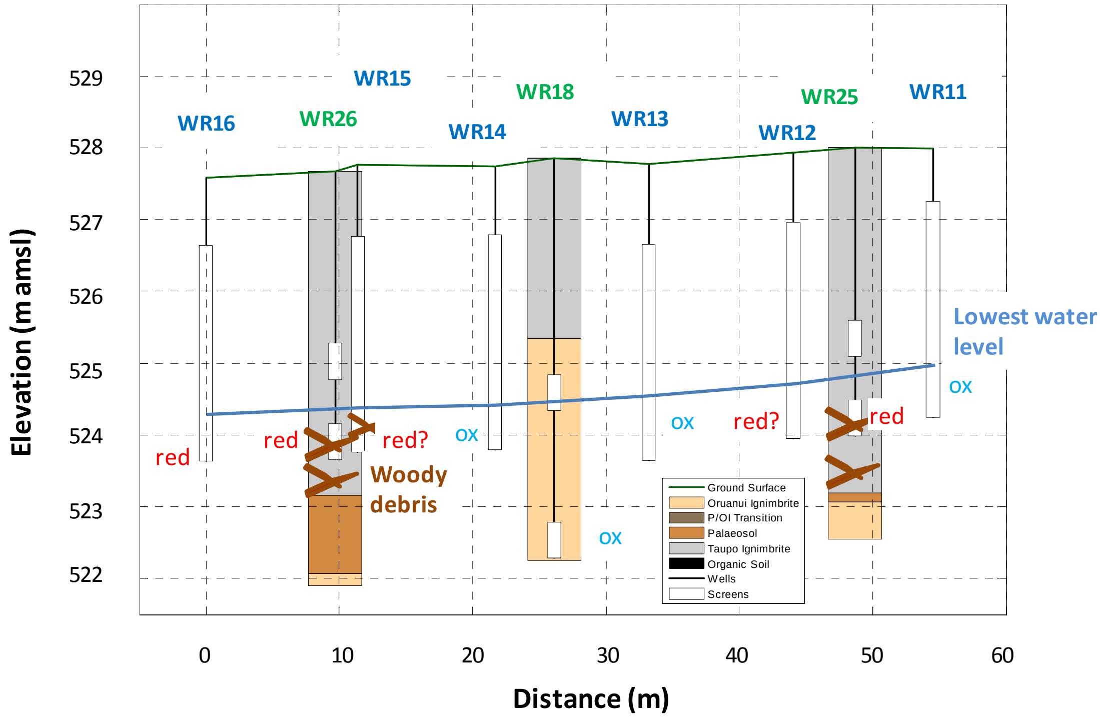


Figure 34: Cross-section of the Upper Transect, schematically indicating redox conditions in shallow groundwater.

Redox stratification at the Lower Transect

Given that the redox stratification at the Lower Transect seems to be more affected by groundwater dynamics than at the Upper Transect, schematics are provided separately for low and high water levels (Fig. 35). At low water levels, i.e. when the water level resides in the deeper part of the Taupo Ignimbrite, the distribution of reduced groundwater largely reflects the distribution of woody debris. Apart from all locations where woody debris was documented, reduced groundwater presumably also occurred at a couple of locations nearby (WR16, WR12). At high water levels, oxidised groundwater seems to prevail near the top of the saturated zone apart from the north-eastern end of the transect where the oxidised zone may be very thin or non-existing. As in the centre of the Upper Transect, reduced groundwater appears to occur substantially higher up in the profile than woody debris (WR25) or even in its absence (WR11, WR13). It has been hypothesised that lateral input of reduced groundwater from upslope locations may be the reason for reduced groundwater dominating the monitored depth range at WR11, WR25, and to a lesser degree at WR13.



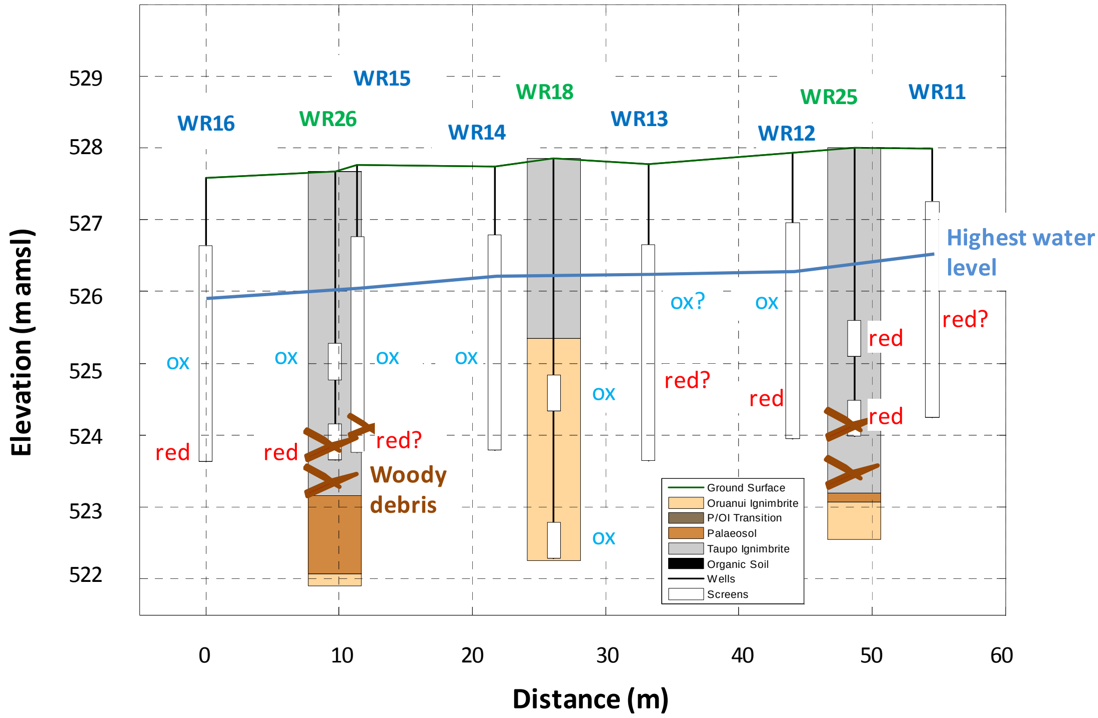


Figure 35: Cross-sections of the Lower Transect, schematically indicating redox conditions in shallow groundwater under low and high water level conditions.

4.2.4 Groundwater nitrate nitrogen vs. estimated root zone losses

The overall mean nitrate nitrogen concentration of all 682 groundwater samples analysed during the 6-year period from November 2004 to December 2010 was 2.07 mg/L. Assuming this mean concentration best describes the concentration of recharging groundwater and using the annual recharge volume estimate of 697 mm as derived from local climate data (Appendix I), mean annual NO_3-N input from the vadose zone can be estimated as 14 kg/ha[3].

Using point-scale groundwater data from the Spydia facility, Barkle et al. (2010) estimated annual total N input into the saturated zone to be 13 or 21 kg/ha, depending on the estimation method used. All of these estimates are markedly higher than the OVERSEER (Ver. 5.4.8) prediction for that site of 9 kg N/ha/year (Betteridge and Power, AgResearch, pers. communication, 2010).

As the circumstantial evidence outlined above additionally suggests that the mean nitrate concentration of the data set has already been reduced by groundwater denitrification, it would appear that the actual leaching losses from the root zone may have been substantially higher than estimated by OVERSEER.

[3] Using the median NO_3-N concentration of 1.53 mg/L instead of the mean concentration would still result in an annual total of 11 kg/ha. However, while the median is the most appropriate estimator for a 'typical' concentration in a temporal sense, the arithmetic mean is the more appropriate estimator for the 'average' concentration required to calculate mass flux.

4.3 Effect of well screen length and position

The potential effect of well screen length and position is often ignored when monitoring data from multiple locations are compared. We demonstrate the relevance of the issue here by reviewing the spatial and temporal variability in the water column thickness that was sampled with the WTW set-up and highlight potential implications. We then discuss the effect of well screen length and position on the monitoring data from a selection of water table wells.

Spatial and temporal variation of the water column thickness sampled

Uncertainty at the time of well drilling about the exact water level location and the difficulty of manually installing deeper wells are amongst the reasons for the spatial variation in the thickness of the groundwater zone sampled by the water table wells (Fig. 36). The thickness additionally varies temporally as the water level rises or falls within the well screen range, while the base of the well screen is located at a fixed depth (see Figs. 34 and 35). How these factors affect the time series data sets from individual wells additionally depends on the specific conditions at each well location, particularly the degree and temporal stability of groundwater chemistry stratification.

As summarised in Figure 36, at the Lower Transect there was little variation in the thickness of the water column present in each well at any one sampling date (< 0.5 m) and relatively little variation over time. At most sampling dates, the water column in each well was between 1 and 2 m thick. Both, the variation between wells, as well as the variation over time was substantially greater at the Upper Transect. At individual sampling dates, the water column thickness varied between the wells of the Upper Transect by between 0.6 and 3.4 m. Over time, the water column thickness of individual wells varied by between 1.4 and 4.1 m.

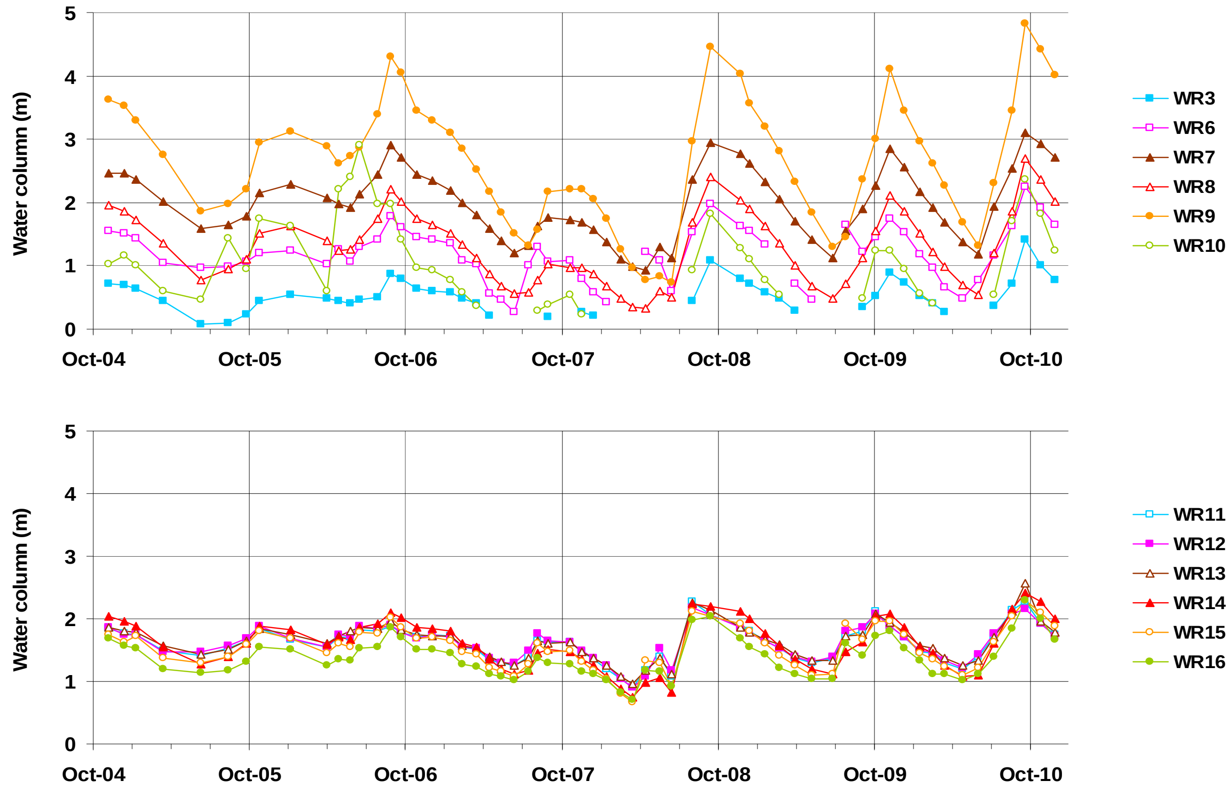


Figure 36: Water column thickness in each well at each sampling date.

Relevance of varying water column thickness

Whenever there is a vertical stratification of the groundwater chemistry, the depth to which a WTW penetrates the saturated zone at a given well location and sampling date will affect the resulting data set.

Reasons for vertical stratification of NO_3-N concentrations in shallow groundwater include:

1. Temporal variation of vertical input from the vadose zone (e.g. water recharged early in the main recharge period often contains more nitrate than water recharged later in winter);
2. Denitrification occurring below a (fixed) redox boundary (e.g. oxidised groundwater occurring above the depth of a resident electron donor, but reduced groundwater below);
3. Presence of different groundwater flow lines originating from upslope areas with different inputs (e.g. due to different land use intensity) and/or different degree of denitrification occurring along the lateral flow paths (e.g. due to patchy distribution of electron donor).

The effect these processes individually and collectively have on groundwater chemistry stratification varies over time. A stable stratification will only occur where one process that shows little temporal variation is the main cause for the observed groundwater stratification (e.g. denitrification occurring below fixed redox boundary).

While the first two processes listed above are most relevant when water table wells are located near groundwater recharge sites, the latter is particularly relevant closer to discharge sites, where different groundwater flow lines can converge at shallow depth. The groundwater chemistry of Lower Transect water table wells is consequently more likely to be affected by lateral groundwater flow than that of the Upper Transect wells.

We used the scatter plots and corresponding regression equations presented in Appendix II to ascertain whether there was a consistent relationship between NO_3-N concentration and water column thickness at any of the individual wells. When considering the entire monitoring period, water column variation accounted only in two data sets for more than 25% of the variation in NO_3-N concentrations (R^2 = 0.40 for positive correlation at WR16, R^2 = 0.27 for negative correlation at WR11). This observation suggests that at most locations groundwater stratification is either absent (i.e. homogeneous groundwater quality in the sampled water column) or variable over time (inhomogeneous groundwater quality, but depth profile changing over time). In a couple of instances, correlations were stronger during the latter part of the monitoring period, as outlined in the discussion of individual data sets below.

While no wells were specifically installed for that purpose, some conclusions regarding the effect of well screen length and position can also be drawn by comparing data from WTWs with those from MLWs located nearby (see Figs. 34 and 35). Charts containing nitrate nitrogen data for the period when both well types were sampled are presented in Appendix III.

Effect of well screen length and position on data from individual wells

The fact that **WR3** had the highest mean nitrate concentration of all water table wells is partly due to its short screen length and its screen position. The similarity of nitrate concentrations measured at WR3 and at the neighbouring, slightly deeper well WR22-1 (Appendix III) demonstrates that there was very little vertical stratification in that depth range (see Fig. 34). However, there was evidently strong groundwater chemistry stratification between WR22-1 and the deeper well WR22-2 (Fig. 26). With 1.5 m length, WR3 had the shortest screen of all WTWs and is located such that it draws only oxidised and nitrate-bearing groundwater from the uppermost part of the saturated zone, on average only from the top 0.5 m (Fig. 36). Had a deeper WTW been installed at this location, allowing sampling of groundwater to a more typical average depth of 1.5 m below the water table, measured nitrate concentrations would have been lower as the longer screen would have reached below the redox boundary into the reduced groundwater sampled at WR22-2.

The paucity of samples from WR27 (Appendix III) and the location of that single well in the Oruanui Ignimbrite do not allow drawing firm conclusions regarding the WTWs **WR7 and WR8**, which have long screens that are entirely located in Taupo Ignimbrite (see Fig. 34). However, as outlined in Section 4.2.2, these wells seem to draw groundwater that is reduced for most of the year even close to the top of the saturated zone. As nitrate concentration stratification only seems to occur during brief periods (see also Appendix III), the exact well screen length and position will have only negligible effects on monitoring data from these two locations.

In spite of **WR9** being screened over 6 m, its very stable nitrate concentrations were quite similar to those of WR21-3, the deepest well of the adjacent WR21 cluster (Appendix III). In agreement with this observation, the data from the few sampling dates for which data from the shallower WR21 wells was also available suggests that there is relatively little vertical stratification at this site. Monitoring results from this location should therefore be rather insensitive to well screen dimensions.

In the Lower Transect, **WR16** and to a lesser degree also **WR15** seem to be drawing groundwater across the redox boundary evident in the data from WR26-1 and WR26-2 (Figs. 28 and Appendix III). The temporally varying proportions of deeper reduced and upper oxidised groundwater presumably explain the positive correlation between groundwater levels and nitrate concentrations found at WR16 (R^2 = 0.40, Appendix II). A water table well penetrating deeper into the saturated zone would thus yield lower nitrate concentrations and a shorter one higher concentrations. Accordingly, WR16 data (from spring 2008) suggest that nitrate concentrations near the top of the saturated zone were higher than those measured at WR26-1, where the screen begins approx. 75 cm below the highest groundwater level (Fig. 35).

While being more variable and having generally higher nitrate concentrations than WR9 and adjacent WR21 at the Upper Transect, **WR14, WR13** and WR18 in the centre of the Lower Transect also do not appear to have a consistent vertical stratification (Fig. 27, Appendix II and Fig. 31). Monitoring data from these locations should therefore be relatively unaffected by well screen dimensions. However, similar to WR11 discussed below, a tentative negative correlation between nitrate concentration and water level (R^2 = 0.28) was observed at WR13 during the period 2008 to 2010.

While nitrate concentration and water level were uncorrelated at **WR12**, a tentative negative correlation (R^2 = 0.27) was found at **WR11** (Appendix II). The scarce information available from WR25 indicates that even the shallower well WR25-1 already samples reduced groundwater with a chemical composition similar to the groundwater sampled at the deeper well WR25-2. The higher concentrations of groundwater sampled at WR11 and the DO profile established in June 2011 suggest that oxidised and nitrate-bearing groundwater can occur near the top of the saturated zone. However, the observed negative correlation demonstrates that nitrate concentrations fall with rising water level. Lateral influx of shallow, reduced groundwater from upslope locations is one mechanism that could explain this pattern. With R^2 = 0.51, the negative correlation was almost twice as strong for the period 2008 to 2010 than for the entire monitoring period (R^2 = 0.27). Annual water level amplitudes during these three years were greater than observed previously, largely due to higher peak values in spring (Fig. 33). This pattern reflects the particularly high difference between rainfall and actual evapotranspiration during the winter months of these years (see Appendix I).

Groundwater sampling strategies

The most appropriate sampling strategy, including well screen length and position, depends on the purpose of the sampling. If the effect of recent land use on recharging groundwater is the primary concern, sampling directly at the top of the saturated zone with a short well screen is most appropriate. The thickness of the groundwater column sampled should be standardised across sampling locations and sampling dates to avoid complications arising from possibly existing vertical water chemistry stratification. The well set-up should consequently allow sampling wherever the top of the saturated zone is located at any one point in time. A series of short well screens in fixed depths may be sufficient at sites with little water level variation, but a more flexible set-up is preferable at sites with a more strongly varying water level.

Since 2007, Lincoln Ventures has used the so-called '*Childs Test*' (Childs, 1981) as a simple field indicator of redox conditions in the saturated zone and this approach has since then also been adopted by Waikato Regional Council (Hadfield, 2009). This field test allows detecting ferrous iron in a borehole sample through a red colour response. Knowing where the stratum is sufficiently reduced for ferrous iron to occur facilitates placement of well screens specifically in 'oxidised' versus 'reduced' zones and thus helps to avoid undesirable screen installations across redox boundaries. It should be noted however, that the location of a redox boundary in a profile can vary with time. In particular, material from the base of the Taupo Ignimbrite stratum (containing woody debris) has been found to contain ferrous iron at all coring dates apart from those that took place in winter following significant groundwater recharge. Recharge can reduce the ferrous iron concentration in a stratum by two processes. Firstly, recharge with oxidised water can result in the oxidation of ferrous ion to ferric ion *in situ*. Correspondingly, orange-brown precipitates have been observed in some boreholes and wells after significant groundwater recharge. Secondly, due to its high mobility, ferrous iron can get displaced from the Taupo Ignimbrite stratum by the influx of recharging groundwater. This example demonstrates that the '*Childs Test*' is an easy to use method to locate a redox boundary, but one needs to be mindful of the possibility of changes with time.

Sampling of deeper groundwater using a single well with a longer well screen at one fixed location will usually yield less noisy time series than sampling directly at the top of the saturated zone. Long-term trends may therefore be easier to detect. Such samples will inherently integrate over different recharge areas and incorporate the effect of processes that may have occurred along the groundwater flow paths to the well screen, e.g. denitrification. They are consequently less suitable for the establishment of cause-effect relationships, but can be used to trigger more detailed investigations to protect a particular water body. However, due to the generally long lag times, monitoring of deeper wells is not sufficient for an adaptive management approach.

5 REFERENCES

Barkle G.F., Wöhling Th., Wall A., Moorhead B., Clague J. (2010) Estimating the Nitrate Load from the Root Zone to Groundwater. In: *The New Zealand Hydrological Society Conference*, 7-10 December 2010, Dunedin, New Zealand. p 187-188.

Barkle, G.F., Wöhling, Th., Stenger, R., Mertens, J., Moorhead, B., Wall, A., and J. Clague (2011) Automated Equilibrium Tension Lysimeters for Measuring Water Fluxes through a Layered, Volcanic Vadose Profile in New Zealand. *Vadose Zone Journal* 10:747-759, doi:10.2136/vzj2010.0091.

Betteridge, K. and I. Power, AgResearch, pers. communication, 2010.

Childs, C.W. (1981) Field tests for Ferrous Iron and Ferric-Organic Complexes (on Exchange Sites or in Water-soluble Forms) in Soils. *Australian Journal of Soil Research* 19: 175-180.

Daughney, C. J.; Jones, A.; Baker, T.; Hanson, C.; Davidson, P.; Zemansky, G.; Reeves, R.; Thompson, M. 2006: A National Protocol for State of the Environment Groundwater Sampling in New Zealand, http://www.mfe.govt.nz/publications/water/national-protocol-groundwater-dec06/national-protocol-groundwater-dec06.pdf

Korom, S.F. 1992: Natural Denitrification in the Saturated Zone: A Review. *Water Resources Research* 28: 1657-1668.

Hadfield, J. (2009) Applying Childs' Test to Groundwater Denitrification Study, Taupo. *The New Zealand Hydrological & Freshwater Sciences Societies Joint Conference*, Whangarei, 23-27 November 2009. p. 101.

Morgenstern, U. 2007. Lake Taupo catchment groundwater age distribution and implications for future land-use impacts. GNS Science Consultancy Rep. 2007/301. Environment Waikato Technical Report 2007/49.

Morgenstern, U., Stewart, M. K., Stenger, R. (2010) Dating of streamwater using tritium in a post nuclear bomb pulse world: continuous variation of mean transit time with streamflow. *Hydrol. Earth Syst. Sci.*, 14, 2289–2301.

Rijkse, W. 2005. Report on Oruanui loamy sand profile, Waihora Station. Prepared for Lincoln Ventures Ltd., Lincoln, NZ.

Stenger, R., Barkle, G., Andler, V.O., Wall, A.W., and Clough, T. (2006) Characterisation of the Vadose Zone in a Lake Taupo Subcatchment. In: *Implementing sustainable nutrient management strategies in agriculture* (Eds L.D. Curry and J.A. Hanly). Occasional Report No. 19. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand. pp 197-207.

Stenger, R., Barkle, G.F., Burgess, C., Wall, A., J. Clague (2008) Low nitrate contamination of shallow groundwater in spite of intensive dairying: the effect of reducing conditions in the vadose zone-aquifer continuum. *J. Hydrol. (NZ),* 47: 1-24.

Stenger, R., Clague, J, Wall, A. (2009) Groundwater nitrate attenuation in a volcanic environment (Lake Taupo, NZ). *Proc. of HydroEco 2009, Austria, April,* p 171-174.

Stenger, R., Woodward, S.J.R., Clague, J., Wall, A. & Moorhead, B. (2010) How the spatial and temporal variation of reduced groundwater zones affects nitrate discharge into a wetland. In: *The New Zealand Hydrological Society Conference*, 7-10 December 2010, Dunedin, New Zealand. p 169-170.

Stumm, W.; Morgan, J.J. 1996: *Aquatic Chemistry*, John Wiley & Sons.

Woodward, S.J.R., Barker, D.J. & Zyskowski, R. (2001) A practical model for predicting soil water deficit in New Zealand pastures. *New Zealand Journal of Agricultural Research*, 44(1): 91-109.

6 ACKNOWLEDGEMENTS

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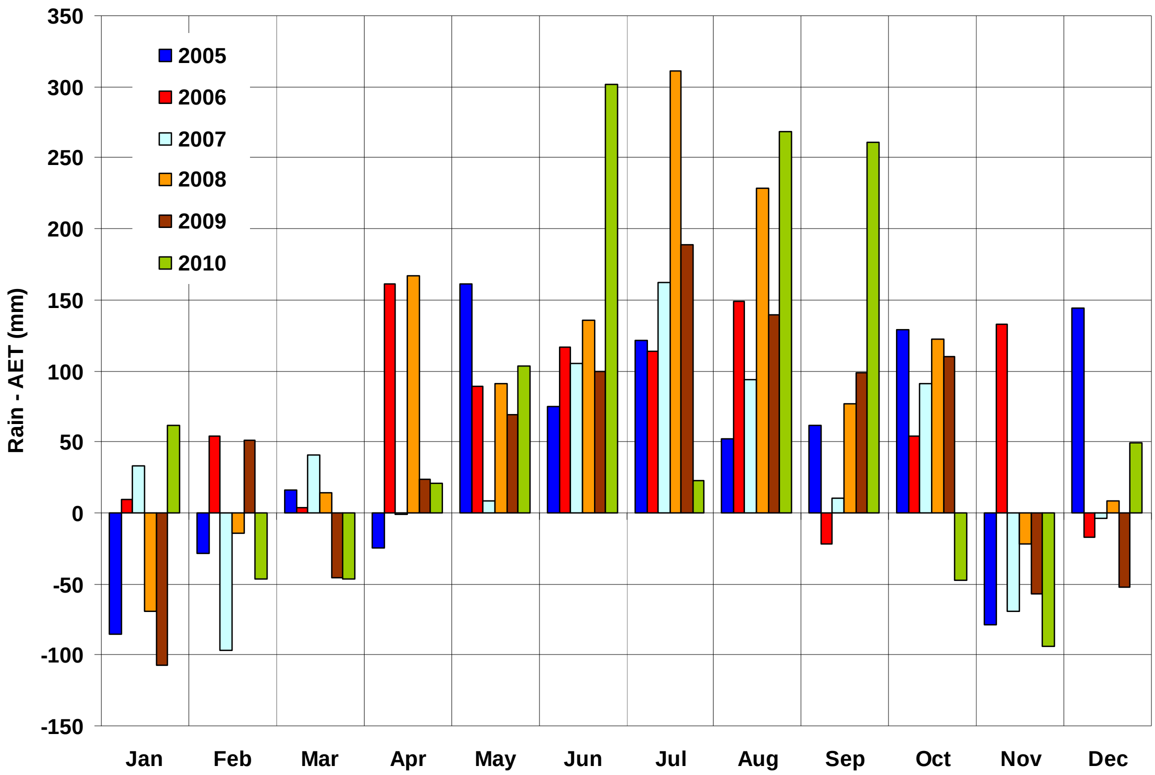
7 APPENDIX I

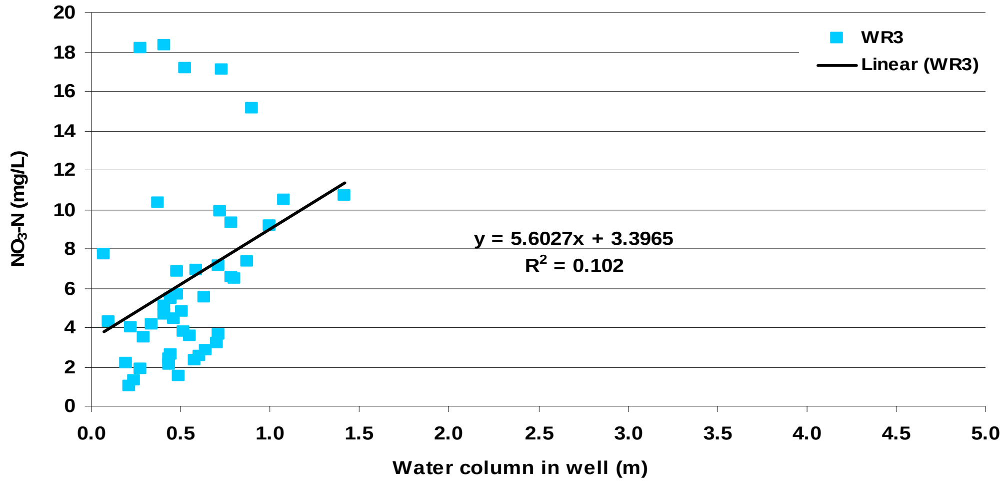
Year	Air temp. (°C)	Rain (mm)	PET (mm)	AET (mm)	Rain - AET (mm)
2005	11.4	1309	815	766	544
2006	11.1	1645	800	800	845
2007	11.3	1183	823	810	373
2008	11.2	1738	842	689	1049
2009	10.7	1306	837	789	517
2010	11.6	1618	847	763	854
median	11.3	1464	830	778	694
mean	**11.2**	**1467**	**827**	**770**	**697**
stdev	0.3	228	18	43	257
CV	2.7	16	2	6	37
min	10.7	1183	800	689	373
max	11.6	1738	847	810	1049
range	0.9	555	47	121	676

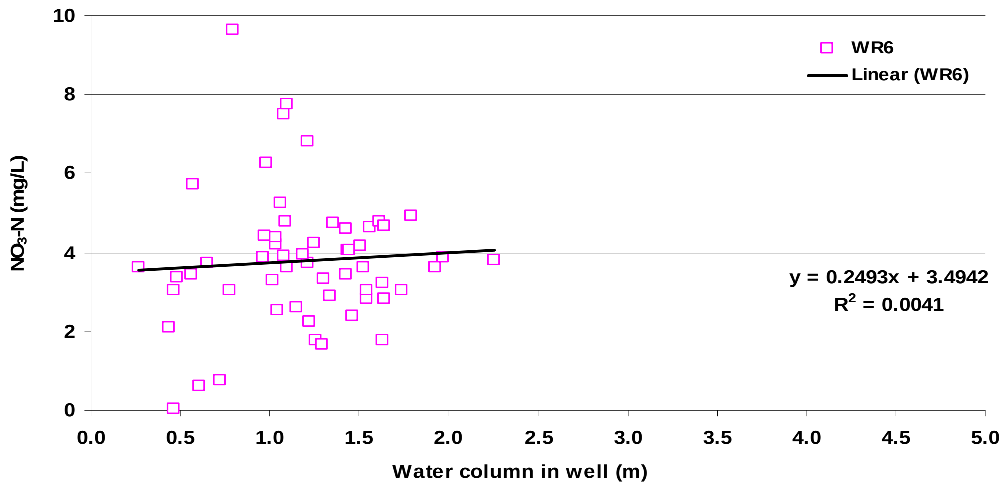
Air temperature and potential evapotranspiration (PET) from Waihora Station weather station; rain measured at Spydia vadose zone facility; actual evapotranspiration (AET) calculated following Woodward et al. (2001).

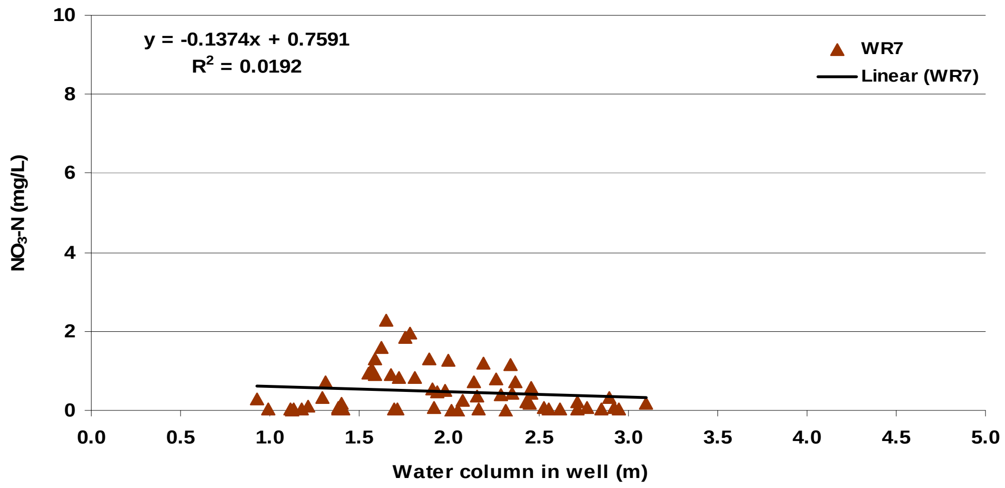


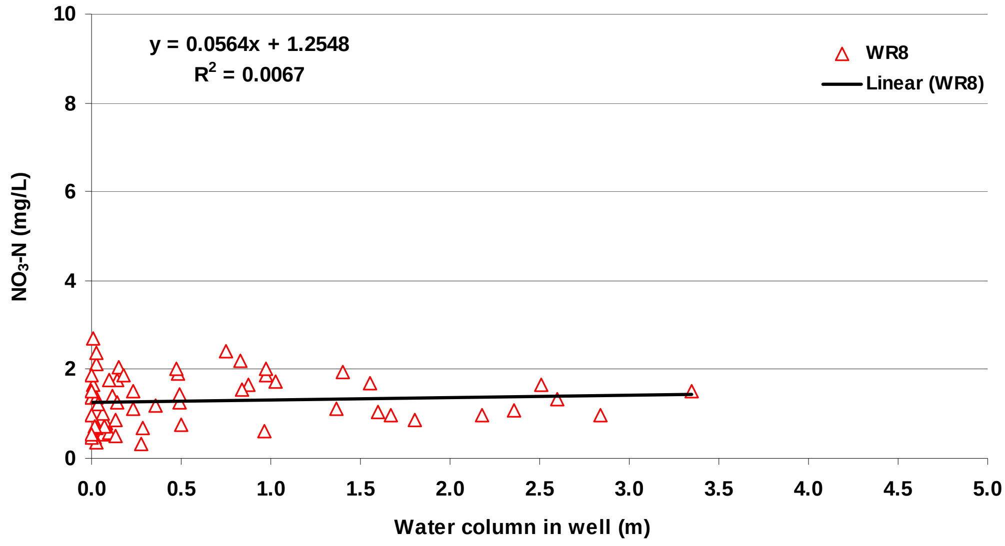
Monthly difference between rainfall and actual evapotranspiration (AET) for the 2005 – 2010 period.

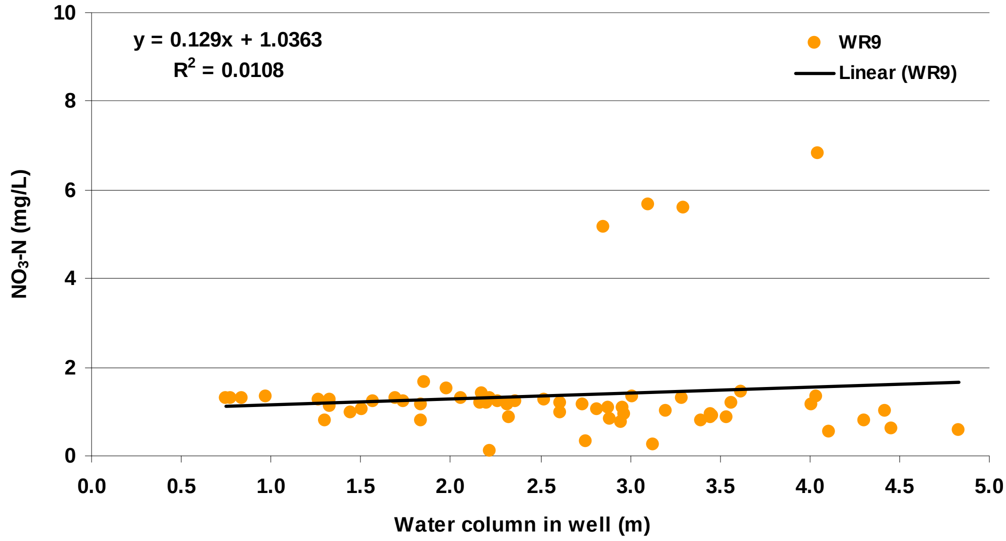
8 APPENDIX II

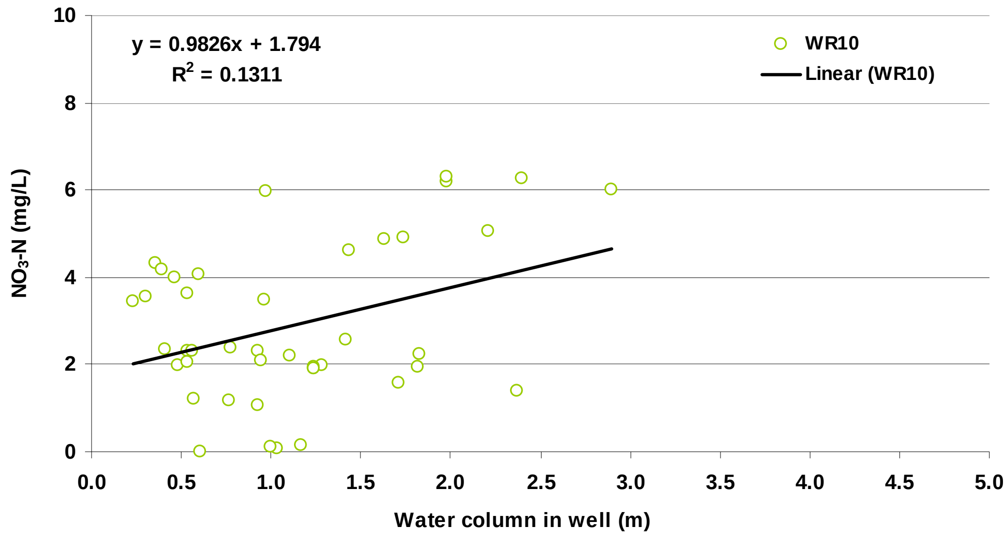




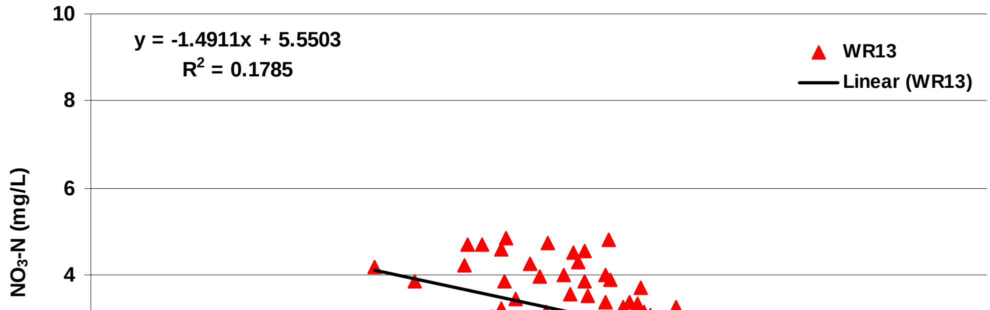



y = 0.0564x + 1.2548
R^2 = 0.0067
WR8
Linear (WR8)
NO_3-N (mg/L)
Water column in well (m)


y = 0.129x + 1.0363
R^2 = 0.0108
WR9
Linear (WR9)
NO_3-N (mg/L)
Water column in well (m)

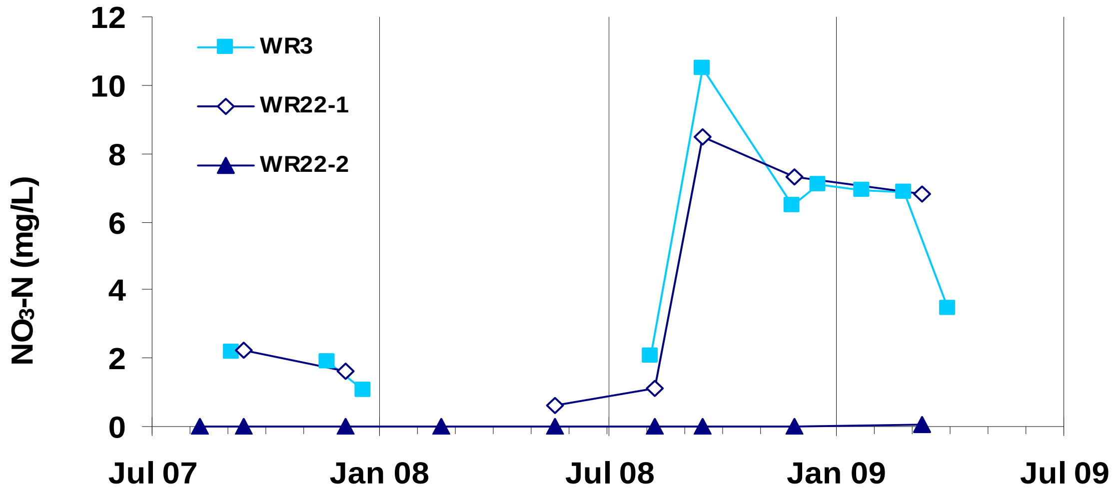

y = 0.9826x + 1.794
R^2 = 0.1311
WR10
Linear (WR10)
NO_3-N (mg/L)
Water column in well (m)


y = 2.4747x - 2.248
R^2 = 0.3995
WR16
Linear (WR16)

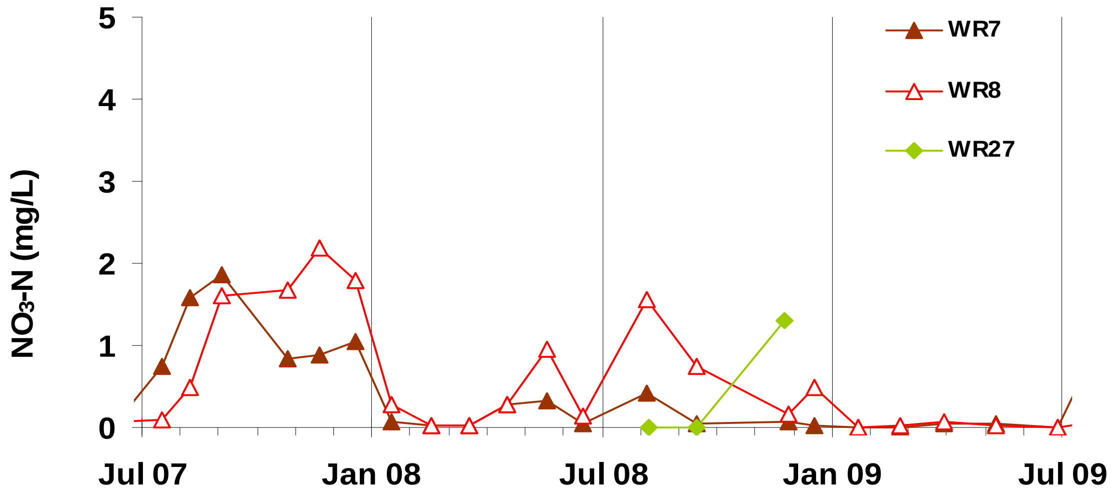

10
8
6
4
y = -1.4911x + 5.5503
R2 = 0.1785
WR13
Linear (WR13)
NO3-N (mg/L)

9 APPENDIX III

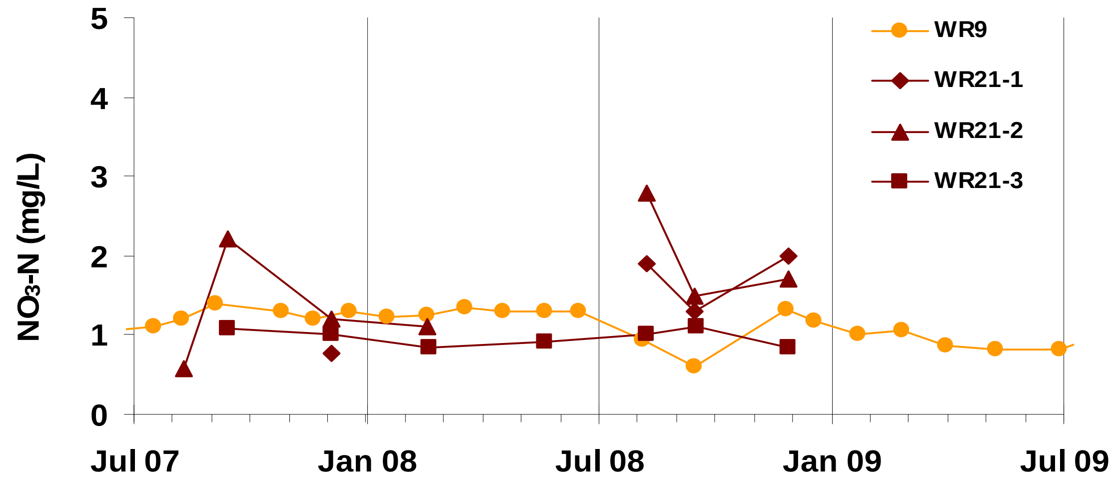
Comparison of WTW and MLW nitrate nitrogen data



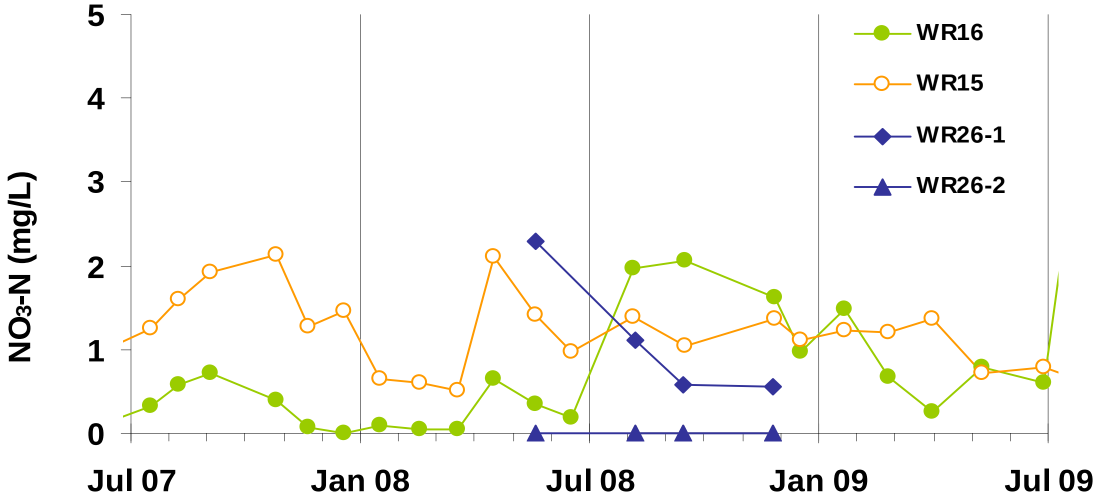
NO3-N (mg/L)
WR3
WR22-1
WR22-2
Jul 07
Jan 08
Jul 08
Jan 09
Jul 09

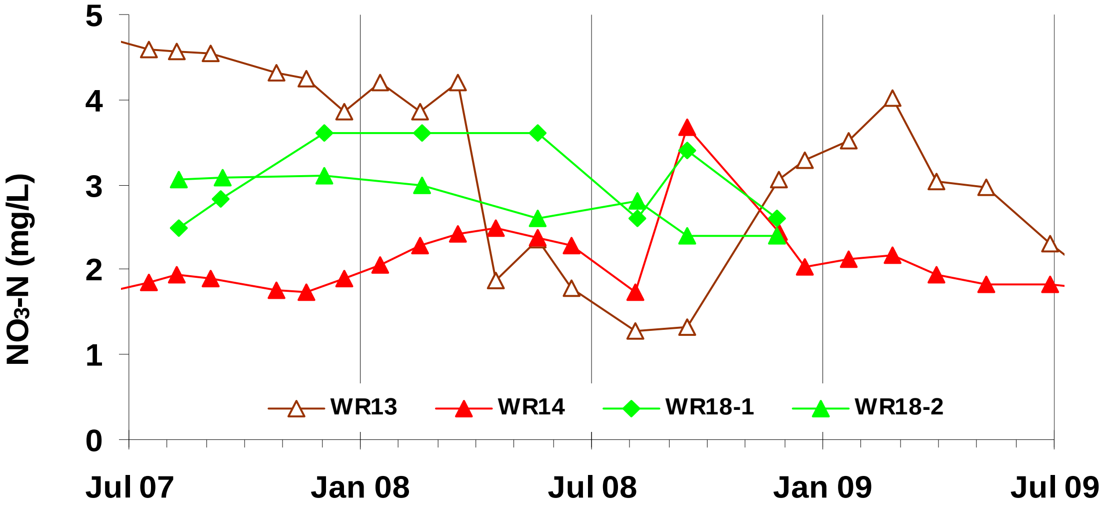


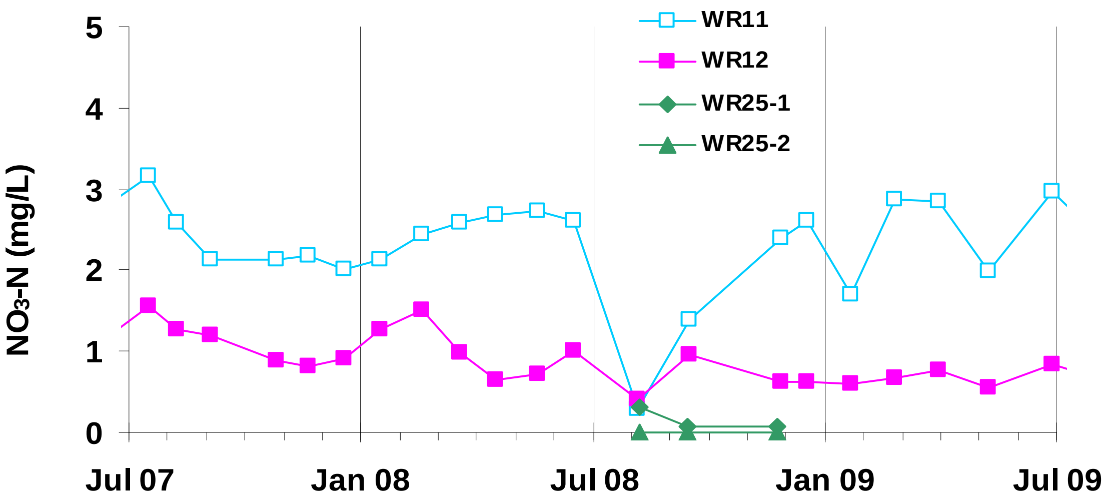
NO3-N (mg/L)
WR7
WR8
WR27
Jul 07
Jan 08
Jul 08
Jan 09
Jul 09



NO3-N (mg/L)
WR9
WR21-1
WR21-2
WR21-3
Jul 07
Jan 08
Jul 08
Jan 09
Jul 09


NO3-N (mg/L)
0
1
2
3
4
5
Jul 07
Jan 08
Jul 08
Jan 09
Jul 09
WR16
WR15
WR26-1
WR26-2


NO3-N (mg/L)
0
1
2
3
4
5
Jul 07
Jan 08
Jul 08
Jan 09
Jul 09
WR13
WR14
WR18-1
WR18-2


NO3-N (mg/L)
0
1
2
3
4
5
Jul 07
Jan 08
Jul 08
Jan 09
Jul 09
WR11
WR12
WR25-1
WR25-2